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The
ENCYCLOPEDIA
of
SPECTROSCOPY

Edited by

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PREFACE

So stimulating and gratifying were the experiences in "calling the signals" for the team of experts who created the "Encyclopedia of Chemistry" (1957) and the "Supplement" (1958) that the same idea of encyclopedic coverage and integration of scattered and diversified subject matter in other rapidly expanding areas of science seemed a most logical sequel and an invitation to further useful service. An incidental bonus from experiences in putting Chemistry between the covers of a single volume plus a Supplement was the revelation of a number of more clearly specialized topics, each of which by virtue of vigorous growth and resultant scattered sources of current information was a choice candidate for this same procedure of collecting, organizing, presenting in brief but lively form, and integrating into a 1960 unified reference mosaic.

Two long-known but ever new examples of instrumentation for observation, identification and analysis not only by chemists but by scientists in many other disciplines, stood out among many possibilities as being ripe for just such a treatment. Which should we choose for the first effort—spectroscopy or microscopy? When outlines were prepared, the recent literature surveyed, and the wishes and opinions of well-qualified scientists sought, it became clear that both of these two instrumental areas, each with a multiplicity of different techniques, were growing vigorously from classical origins and early histories often in parallel channels, often intimately in contact or even almost inextricably interwoven (such as infrared microscopes for microspectrophotometers, electron microscopic sources for microprobe x-ray spectrometry or spectroscopic monochromators for microscopy). Both are characterized by recent development of entirely new techniques and new instruments, which in turn have served to rejuvenate to an astonishing degree such relatively antique methods as those employing the light microscope like that built by Leeuwenhoek more than three centuries ago or Bunsen's emission spectroscope a century ago.

It is not surprising, then, that we have presided at the birth of twin one-volume encyclopedias. With the same general ideas and ideals which characterized the earlier chemical encyclopedias, a team of spectroscopists and another team of microscopists were called upon to create these two new encyclopedias simultaneously in less than two years. These are to be sources of information for all inquisitive scientists—novices and experts—and intelligent laymen to look to for a picture of two indispensable groups of testing and research tools and the scientific structures built with them, as complete and carefully blended as humanly possible.

A considerable number of authorities from other countries accepted the invitation to participate in the Encyclopedias of Spectroscopy and Microscopy; they have made notable contributions and given a world-wide scope to this undertaking. As an example there is an article from Holland in which six kinds of microscopy are applied to every kind of fiber, pulp and paper, and plastic.

Of course single, extremely well-trained, and experienced authors might be able to write better integrated texts in unified style on these subject areas, avoiding duplication and gaps. But it is difficult to imagine, in these days of clinical instead of individual approach to such projects, that a single author or a small group of co-authors could present

Preface

twenty-three kinds of spectroscopy or twenty-six kinds of microscopy, applied in manifold ways in chemistry (especially analytical spectra and chemical spectroscopy), physics, all branches of biology, medicine, metallurgy, geology and mineralogy, ceramics, agronomy, electrical engineering and electronics, the petroleum, chemical, pharmaceutical and other industries.

It is obviously difficult to unify and integrate over three hundred articles on spectroscopy and microscopy written by scores of distinguished scientists. But each one represents the knowledge, experience and spirit of a true spectroscopist or microscopist who might be in any one of the diverse fields of science just mentioned. For each scientist chooses one or more techniques to apply uniquely to a research program, and though he be a chemist or biologist or metallurgist, he masters the instrumental tool to meet a specific need, and so becomes a creative spectrographer or micrographer—not just a technician or a mere puncher of buttons on an automatic machine which registers data, computes results and controls processes on stream. How could a compiler of a text know the inner thoughts and hopes of an electron micrographer who in the far North built an igloo with a hole in the roof to collect snow crystals for the study of the nuclei which caused them to form in fantastically beautiful hexagons? Or how could he know that the first idea of an electron microscope, never recorded in a publication, probably came 30 years ago to a distinguished electrical engineer in Germany under the compulsion of the anguished hope of seeing the virus which caused dreaded polio in his 3-year old child? For somehow conveyed in each of the articles is not only entirely new and previously unpublished material, but also an individuality and the evidence of dedication, and the spirit of cooperation which transcend any deficiencies arising from a mosaic coverage of topics. The two collections of articles speak for themselves, and eloquently for the modern status of microscopy and spectroscopy as professions, as was so convincingly stressed in an *Analytical Chemistry* (1960) staff report of an American Chemical Society Symposium on Microscopy.

These are encyclopedias with topics arranged alphabetically, first according to principal kinds of microscopy (26) or spectroscopy (23), and then under each of these the various aspects of history, theory, instrumentation, techniques, interpretations and applications of each method, which taken together cover the topic as completely as possible. Carefully chosen lists of general and cross references and illustrations, it is hoped, will add greatly to the value and usefulness of these two volumes, in presenting facts and in guiding the reader to more exhaustive sources of information.

The Editor is indebted first of all to the considerable number of eminent scientists who have generously, patiently and loyally given vitally important advice and have contributed to these twin Encyclopedias from one to ten or more authoritative articles (Fulton, Humphreys, Jarrell), because of their recognition of the need of this service to science and their willingness to accept largely intangible rewards for time and effort. As experts in particular areas, most of these collaborators have been continuously bombarded in recent years to write books or compose contributions to encyclopedias, symposia, reviews, and lecture tours. Their acceptance without grumbling in the face of such demands proves that they are true friends as well as leaders of science. The lists of contributors in the front pages of the two Encyclopedias are indeed Rolls of Honor.

The planning, organization and editing (not to mention the writing of twenty-five articles to fill in gaps, several at the last minute) have somehow been carried out almost entirely with the able and loyal help of two secretaries serving consecutively, Mrs. Ruth Tuite (1958–59) and Mrs. Claretta Metzger (1959–60), who kept the extensive correspondence

and files in order. These volumes will always represent for the Editor twin beacon lights which will appear concurrently with retirement after 33 years of active teaching and research at the University of Illinois. Perhaps the new turn in the road may be illuminated hereby for continuing creative usefulness in writing, editing and research, primarily in order to measure up to the hope and belief of the Publishers in the potential value of these Encyclopedias; and, after 41 years to the abiding faith of wife and family in the conviction that retirement need not mean idleness and stagnation; and to the loyal devotion of the hundred Ph.D.'s whose minds and hearts and hands have been hopefully guided into the pathways of research. With such challenges, in the words of a great poet, Dr. Henry Van Dyke:

Let me but live my life from year to year
 With forward face and unreluctant soul;
 Not hurrying to, nor turning from the goal;
 Nor mourning for the things that disappear
 In the dim past, nor holding back in fear
 From what the future veils; but with a whole
 And happy heart, that pays its toll
 To youth and age, and travels on with cheer.
 So let the way be up the hill or down
 O'er rough or smooth, the journey will be joy;
 Still seeking what I sought when but a boy—
 New friendship, high endeavor and a crown.
 My heart will keep the courage of the quest
 And hope the road's last turn will be the best.

G. L. CLARK

November, 1960

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ABSORPTION SPECTROSCOPY (SPECTROPHOTOMETRY)— VISIBLE AND ULTRAVIOLET

ANALYTICAL ABSORPTION SPECTROMETRY

Absorption spectrometry is one of the very important kinds of methods of chemical analysis. The principle underlying this method is the absorption of radiant energy by substances. At some wavelength(s), a given substance absorbs in a given way and to a particular extent. The nature of the absorption provides information about what the substance is and the extent of the absorption provides information about the amount of the substance. A curve coordinating absorptive power with spectral region is known as an absorption spectrum. Spectral regions absorbing more than others are known as absorption bands.

Like various other physical properties, the absorption of radiant energy by substances may be of interest in a number of areas. The primary concern here is analytical rather than physical chemistry.

A wide range of the electromagnetic spectrum is involved. Currently, interest ranges from short x-rays to long microwaves. The approximate ranges assigned to the respective regions follow: x-rays, <1 to 100 angstroms (Å); ultraviolet, 10 to 400 millimicrons (mμ); visible, 400 to 700 millimicrons (mμ); infrared, 0.7 to >800 microns (μ); and microwave, 0.1 to 1,000 centimeters (cm). Thus far the principal analytical applications are in the range of 0.2 to 25 μ.

In referring to particular regions of the electromagnetic spectrum wavelength (λ), frequency (ν), and wavenumber (ν') are used. Each has some merit. They are related as follows:

$$\frac{1}{\text{wavelength (cm)}} = \text{wavenumber (cm}^{-1}\text{)}$$

$$= \frac{\text{frequency (sec}^{-1}\text{)}}{\text{speed of light (3} \times 10^{10} \text{ cm sec}^{-1}\text{)}}$$

Then, for example, 500 mμ = 20,000 cm⁻¹ = 600 f (fresnels).

Various transmission terms relate to the rectilinear passage of homogeneous radiant energy (i.e., single frequency) through a medium having plane, smooth, parallel sides, or through a cell having windows of such material and containing a homogeneous solution.

In the schematic diagram of Fig. 1, P_1 represents the radiant energy incident upon the first surface of the medium (e.g., face of an absorption cell), P_0 that entering the sample solution of thickness b and concentration c , P that leaving the solution and incident upon the second surface, and P_2 that leaving the last surface of the medium. Then,

$$T_0 = P_2/P_1 = \text{over-all transmittance (100 } T_0 = \text{percentage transmittance)}$$

$$T_i = P/P_0 = \text{internal transmittance}$$

$$A = \log_{10} P_0/P = \log_{10} 1/T_i = \text{absorbance}$$

For the solution in Fig. 1,

$$T_{0(\text{soln.})} = \text{over-all transmittance of solution and cell}$$

$$T_{0(\text{solv.})} = \text{over-all transmittance of solvent in same (or optically matched) cell}$$

$$T_s = T_{0(\text{soln.})}/T_{0(\text{solv.})} = \text{transmittancy of solute}$$

$$t_s = \text{transmittancy of unit thickness}$$

$$A_s = \log_{10} 1/T_s = \text{absorbancy of solute}$$

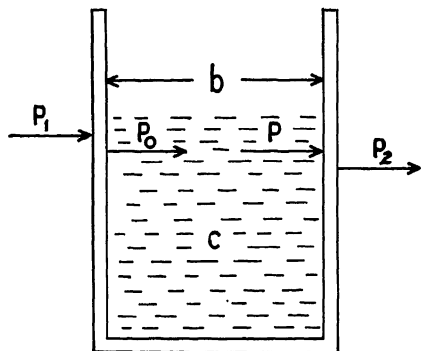


FIG. 1. Passage of a beam of radiant energy through a solution.

$a_s = A_s/bc$ = absorptancy index (for given thickness and concentration)

a_M = molar absorptancy index (if $b = 1$ cm., and $c = 1$ mole/liter)

$1 - T_s$ = absorptancy (no symbol)

Various other symbols and terms have been used. The most common are: A (absorbance) = E (extinction) = D (optical density); a (absorbance index) = absorptivity = k (extinction coefficient); and a_M (molar absorptancy index) = ϵ (molar extinction coefficient).

Usage is tending toward dropping the s subscripts recommended by the National Bureau of Standards, and thus not distinguishing between $-ce$ and $-cy$ terms. Consequently, only $-ce$ terms are used henceforth.

Reflection terms concern only incident and reflected radiant flux.

Laws of Absorption. For the absorption of radiant energy by homogeneous, transparent media there are two laws of fundamental importance.

Bouguer's law (often attributed to Lambert) expresses the relationship between absorptive capacity and thickness of an absorbing medium. Each layer of equal thickness absorbs an equal fraction of the radiant energy which traverses it. The absorption varies directly as the logarithm of the thickness. For homogeneous systems there are no known exceptions to this law.

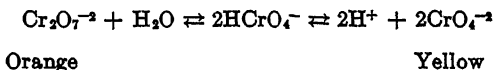
As shown in Fig. 1, P_0 and P are, respectively, the radiant flux incident upon, and emergent from, a solution of concentration c and thickness b . If a layer of unit thickness transmits a fraction t of the radiant energy incident upon it, a thickness b will transmit the fraction t^b . Then $P = P_0 t^b$. This law may be expressed in the form

$$T = 10^{-ab}$$

in which T is the transmittance (P/P_0), 10 is the base of common logarithms, and a is the absorbance index.

Beer's law, as generally stated, expresses the relationship between absorptive capacity and concentration of the solute in a solution. The absorptive capacity is directly proportional to the number of absorbing entities, such as ions or molecules. Then, if c is the concentration of solute, the transmittance for a given thickness is t^c , where t is the transmittance for a solution of the same thickness having unit concentration.

This law applies if the radiant energy is approximately monochromatic, and if the nature of the absorbing species is the same in solutions of different concentrations. It must be kept in mind that the absorbance index, a , depends upon the wavelength of the incident radiant energy. Also any action in the solution, such as ionization, association, or dissociation, which affects the nature of the absorbing species will affect the absorption. A familiar example is the change in color resulting from dilution of a solution of a dichromate with water. The equilibrium involved in this color transformation may be represented by the equation,



Bouguer's and Beer's laws may be combined in the expression

$$T = t^{bc} = 10^{-abc}$$

Then,

$$c = A/ab$$

These relationships show that the measured transmittance (absorbance) is a function of the absorbance index, the cell thickness, and the concentration. Obviously, the numerical value of the absorbance index depends upon the units used in expressing b and c . In addition, the measured quantity (A or T) may depend upon temperature, solvent, spectral band width employed, and wavelength of the illuminating source. The magnitude of the index is a measure of absorptive capacity.

Instruments. Instruments designed for measuring absorptive capacity of substances for radiant energy are variously referred to as spectrometers, photometers, absorptimeters, and spectrophotometers. Terms often used synonymously for absorptimetric methods are absorption spectrometry (spectroscopy), absorptimetry, and spectrophotometry. Measurement of radiant energy (flux) as a function of wavelength is relative. In transmission measurements the standard usually is air (blank beam), or an absorption cell free of the absorbing constituent or containing a known amount of it; in reflection measurements it is some standard surface, such as magnesium oxide.

The essential components of a spectrophotometer are (1) a source of radiant energy, (2) a detector for unabsorbed radiant energy, (3) a monochromator for the isolation of the desired spectral band of radiant energy, (4) an absorption cell, if the sample is a gas or liquid, and (5) in many instruments, a photometer. Fig. 2 is a schematic diagram of the relationship of these components. S is a source; p , a dispersing prism; O , a slit; C , an absorption cell; E , a photoemission cell; and M , a combined amplifier and meter.

In the case of both sources and detectors, it is necessary to select those appropriate to the spectral region in which measurement is to be made. Thus, an x-ray source will not serve in the microwave region, nor a red-sensitive photocell in the vacuum ultra-

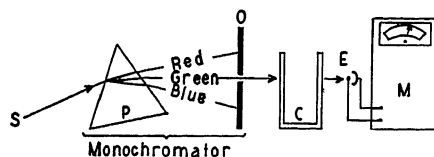


FIG. 2. Essential components of a photoelectric spectrophotometer.

violet. Likewise, the materials of the absorption cell and the dispersing element must be suitable for the wavelengths to be used.

A dispersing element may be a prism or a grating. The former gives nonlinear dispersion and the latter linear. Consequently, with prism instruments it is necessary to have a changing slit width in order to isolate a spectral band of constant width throughout a given spectral region.

Fig. 2 indicates that essentially spectrophotometers are relatively simple. In practice, however, it was recognized two decades ago that 72 arrangements were possible, considering only the major variations that can be used in the spectral, geometric, and photometric parts of the instruments. In certain kinds of work, especially reflectance of opaque bodies, it is important to know the kind of instrument used. Fig. 3 shows the possibilities.

With improving instrumentation, the range of spectral analytical interest is expanding. Instruments for the vacuum ultraviolet have become available and commercial instruments for the microwave region are awaited. Instruments for the non-vacuum ultraviolet, the visible, and the infrared regions are already indispensable in many laboratories. Of all the possibilities only one has been selected as an example.

Fig. 4 illustrates the versatile Cary Model 14 recording instrument. Its range is from about 186 to 2600 $m\mu$, i.e., from the vacuum ultraviolet into the near infrared region. Fig. 5 shows the parts of the optical system.

The schematic optical diagram of Fig. 5 shows the path of ultraviolet and visible radiant energy through the instrument.

ABSORPTION SPECTROSCOPY—VISIBLE AND ULTRAVIOLET

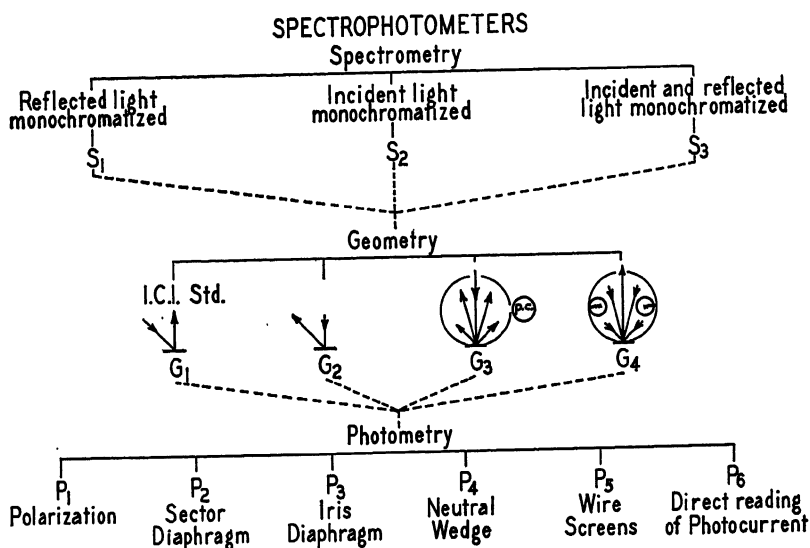


FIG. 3. Diagram showing various spectrophotometric combinations.

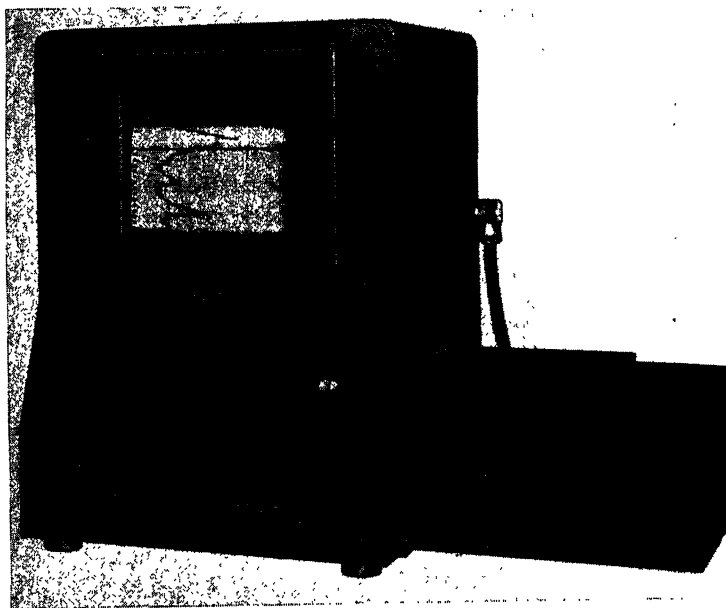


FIG. 4. General view of the Cary Model 14 spectrophotometer.

Radiant energy from the hydrogen lamp *A* or tungsten lamp *C* enters the double monochromator through slit *D*. It is dispersed by the prism *F* and grating *J*; *H* is the variable width intermediate slit. Monochromatic ra-

diant energy leaves through slit *L* and is sent at 30 cps through alternately the reference cell *T'* and the sample cell *T* by means of a rotating semicircular mirror *O* which is driven by a synchronous motor. It alter-

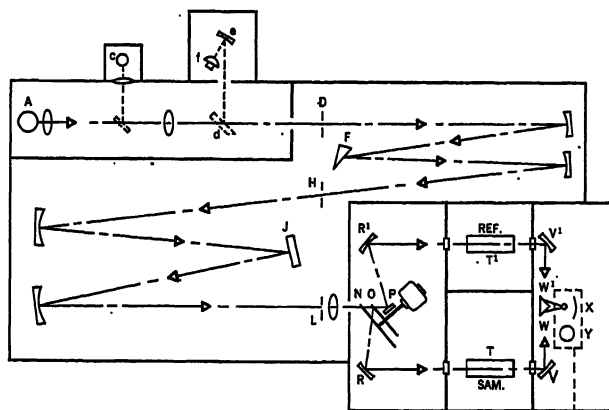


FIG. 5. Schematic optical system of the Cary Model 14 spectrophotometer.

nately reflects the beam to the mirror R and allows it to pass on through to the mirrors P and R' . On the shaft of the synchronous motor is also a chopper disc N which produces a dark interval between each half cycle of the alternation. The beam through the reference cell, consisting of pulses of monochromatic radiant energy at 30 cps, and a similar beam through the sample cell, are directed to the photocell X by the mirrors V , V' , and W , W' . The pulses of the two beams are out of phase with each other so that the photocell receives energy from only one beam at a time.

When the instrument is used in the infra-red region the tungsten light source Y is slid into the place of the phototube X . Radiant energy from the source is divided between the sample and the reference cells, chopped and sent into the monochromator through slit L by the chopper and mirror. Alternate pulses of sample and reference beam are dispersed by the monochromator and directed to the lead sulfide cell f by mirrors d and e . By this system, non-monochromatic infrared radiant energy thermally emitted by surfaces in the chopper unit which would appear in the beams reaching the lead sulfide cell if it were placed at X , is eliminated by the monochromator from the energy to be measured.

Spectrophotometric Data. The data yielded by spectrophotometric measurement depend upon the instrument and its graduation. In some early instruments the swing of a galvanometer, with and without the sample in the incident beam, gave, respectively, a measure of P and P_0 . Current instruments are likely to be graduated directly in terms of T (transmittance), A (absorbance), or $\log_{10} A$. Some instruments have two or more of these scales, with means for shifting from one scale to another. Calculated values may be a (absorbance index), $\log a_M$ or ϵ (molar absorbance index), and $1 - T$ (absorptance).

Actual measurement yields anything from a single photometric value for a single wavelength (frequency or wavenumber) to a curve for a range of wavelengths (frequencies or wavenumbers).

To determine a spectrophotometric curve with a nonrecording instrument, photometric values must be determined at many wavelengths to locate sharp absorption bands. Recording instruments greatly facilitate such measurements.

Fig. 6 shows three quite different spectrophotometric curves for a didymium glass. There are two general interpretations: (1) plotting points at wavelength intervals too far apart will cause increased flattening of the curve as the points decrease in num-

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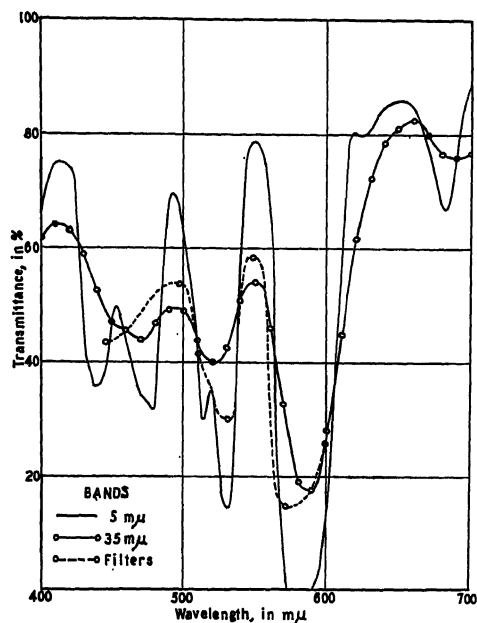


Fig. 6. Transmittance curves for a didymium glass using different spectral band widths.

ber, especially for systems with marked absorption bands; (2) using spectral bands that are too wide similarly smooths out an irregular curve. In Fig. 6 the latter interpretation applies. The continuous curve, without points, was recorded with a band width of 5 $m\mu$, whereas that with the marked points was based on readings with a band of 35 $m\mu$. The discontinuous curve was drawn through points marking the values obtained on a visual photometer with glass filters, the median wavelengths of which located the wavelength points on the graph. The disagreement of the curves is obvious. Each curve is the curve for the glass, for the specific instrumental conditions used..

In plotting spectrophotometric data there is considerable inconsistency. Abscissa values are usually expressed in terms of wavelength, frequency, wavenumber, or log wavelength. This may be attributed partly to the early conditioning of the investigator, and partly to the fact that a given system may be preferable in a given situation. For example, the international system for calculating the

numerical specification of color uses wavelength; in the infrared, analytical chemists use wavelength, but physical chemists are likely to use wavenumber; and many qualitative analysts prefer $\log_2$ wavelength because the lengths of scale used in the ultraviolet, visible, and infrared ranges are then more nearly equal.

Photometric values are usually given as transmittance, absorbance, or $\log_{10}$ absorbance; or, less frequently, as absorbance index, $\log_{10}$ molar absorbance index, or absorptance. As in the case of abscissa values, there are arguments for each of these photometric designations. International (C.I.E.) color values are calculated in terms of transmittance readings. Absorbance values are additive in analytical determinations on polycomponent systems (if Beer's law applies). Log absorbance values give curves the form of which is independent of concentration of solute in the solution. Absorbance index, or $\log_{10}$ molar absorbance index, is much used by organic chemists for comparison of curves.

Fig. 7 shows, for a solution of potassium

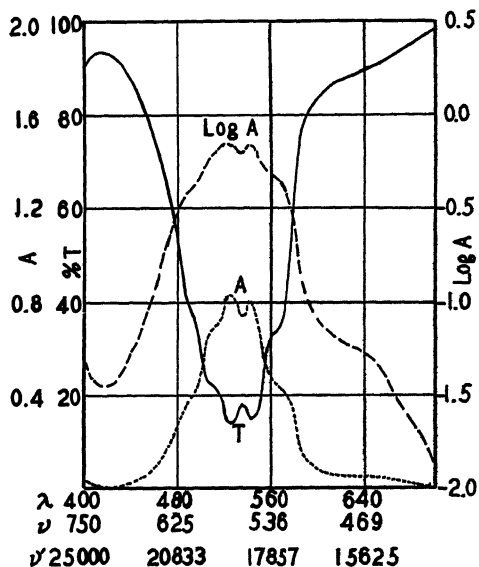


Fig. 7. Spectral curves for a solution of potassium permanganate plotted with three different ordinate and abscissa scales.

permanganate, three scales for the spectral region and three curves for three different photometric scales.

Analytical Applications. For convenience, analytical applications are subdivided on the basis of qualitative and quantitative uses of spectrophotometric data.

Qualitative Uses. Selective absorption of radiant energy results in characteristic curves, with the distinctive parts of the curve in particular regions of the spectrum. The recorded curve in Fig. 6 is a good example in the visible spectrum. Most curves in the infrared region are more striking, although it should be kept in mind that the visible region is just over 0.3μ while the usual analytical infrared range is more than 50 times as broad.

The following examples illustrate some possibilities of basing conclusions regarding qualitative composition of substances upon form and spectral location of curves.

Identification of Substances. For pure substances often the form of the absorption spectrum is very characteristic. Some advertisers of equipment may refer to such a curve as a kind of fingerprint. However, it should be emphasized that a spectrophotometer is a non-discriminatory instrument; that is, for a mixture of two or more absorbing substances the absorption spectrum shows simply the effect of all absorbers. Thus, the curve for a pure substance might be greatly changed by the presence of another substance absorbing in the same region.

These uses generally depend upon finding prominent absorption bands in particular spectral regions. In the absence of significant bands, it may be preferable to compare absorbance ratios for selected wavelengths.

Such general use of absorption spectra has become widespread, especially in the infrared region for organic compounds. Even earlier there was wide adoption of the method in the ultraviolet and visible regions. One dye laboratory has over two million curves in its library collection. The

American Society for Testing Materials has coded for sale nearly 20,000 punched IBM cards for the infrared region and nearly half as many for the ultraviolet region. These may be sorted by machine for comparison with an unknown.

If the curves for an unknown and for a known compound agree closely, identity of composition or structure is indicated strongly, but not confirmed. It is possible for two quite different systems to yield closely agreeing curves, at least over limited spectral regions.

Other Qualitative Uses. There are a number of other uses which are essentially qualitative, although they do not involve identification of substances.

One of these is the study of permanent colorimetric standards for the comparimetric determination of substances, such as residual chlorine in water. Such a standard is designed to be visually equivalent to the unknown. If the systems have substantially superimposable curves, they will match under any kind of illumination. If not, there can be difficulty. Two systems may appear visually identical, under a given illuminant, and yet have quite different curves. If the unknown or permanent standard is dichroic, and the other not, a match may be possible at only one thickness.

Selection of filters to pass or absorb in particular regions of the spectrum is a common problem. Knowledge of the absorption spectra of possible substances is needed.

In this category belongs spectrophotometric evidence on the nature and the course of chemical reactions. Such applications are probably most extensive in biological and organic chemistry, but they are not confined to these areas. Specific examples are adsorption, complexation, hydrolysis, ionic equilibria, ionization constants, kinetics, isomerism, molecular association, polymerization, and solvation. To interpret curves, as in the ultraviolet and infrared regions, one should know the absorptive effects of such factors

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as functional groups, specific structures, and possible chemical transformations.

In the visual region the chemist soon learns to associate different forms of absorption spectra with particular colors. Color is very important in many chemical products and processes. Often the production, or avoidance, of given products, or the control of production and operational processes, is based upon color phenomena. In analytical chemistry especially, one or more of at least the following factors are often very important: stability, pH change, temperature, time of reaction, best chromogenic reagent, order of mixing reactants, state of oxidation, nature of the solvent, and interfering reactions. These effects may be followed by means of absorption spectra.

For a variety of materials there may be established standard specifications of quality

and performance in terms of curves. Such curves serve for comparison of subsequent products. Data may be secured for the standard or desired grades of materials. Then the effects of processing, impurities, and other measurable factors can be determined by comparison with the standard curves. This may lead to change and control of the manufacturing process to achieve permissible tolerances in the products.

Quantitative Uses. Quantitative uses of absorption data depend upon the magnitude of absorption being a function of the concentration of the absorbing species at some wavelength. The following examples are taken from the visible region, but the principles are general, except for the specification of color.

Sensitivity and Range of a Method. A set of curves for a series of solutions of suitable concentrations shows, for the specified thickness, the sensitivity of a method of analysis and the range of concentration to which it may be applied reliably without changing the conditions, such as diluting or concentrating the sample or using different cell thicknesses.

The curves in Fig. 8 show the possibilities for a fairly sensitive colorimetric method. Optimum conditions for making photometric measurements vary with methods of measurement, but it is generally agreed that the transmittance should lie between 15 and 80 %, and preferably a somewhat narrower range. Reference to Fig. 8 shows that this means the concentration of iron to be measured in a 1-cm. cell by this method should be not less than 0.5, nor more than 4 mg./liter. Inasmuch as some methods are capable of measuring much smaller amounts of certain constituents, and some are not nearly as sensitive, the phenanthroline method is considered as one of the better ones.

Another method of evaluating sensitivity is in terms of the molar absorptance index. According to the Bouguer-Beer law, $a_M = A/bc = -\log T/bc$. Referring to Fig. 8, and

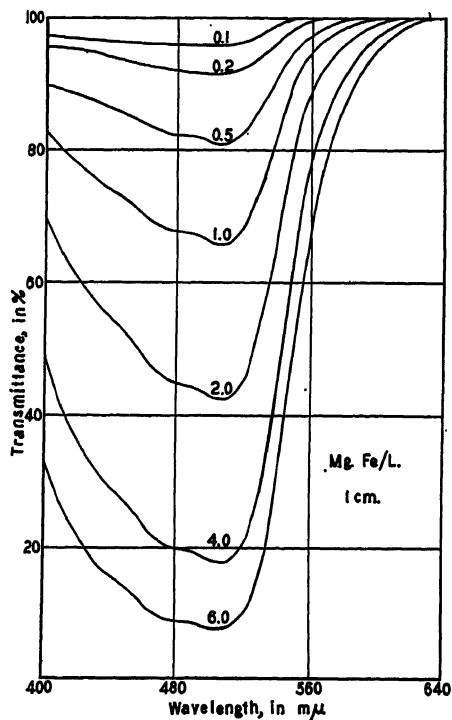


FIG. 8. Transmittance curves for different concentrations of iron complexed with 1,10-phenanthroline.

the curve for 4 mg./liter, T is 0.18 (18 per cent) at 508 $m\mu$. A concentration of 4 mg./liter is 0.0000716 moles and the thickness b is 1 cm. Substitution of these values in the above relationship gives 10,400 as the molar absorbance index. Some systems have a much higher value (20,000 to more than 30,000), but many are much lower.

Conformity of Systems to Beer's Law. A set of curves such as those shown in Fig. 8 serves to test a given system for conformity to Beer's law. Usually transmittances or absorbances are taken at the wavelength of minimum transmittance or maximum absorbance, if there is such a minimum or maximum. This is because here there is maximum sensitivity in the method, and also minimum photometric error for a given error in the wavelength reading. Then one usually plots as abscissas the concentration, and as ordinates the absorbance or the logarithm of the transmittance, on a linear scale, or the transmittance on a logarithmic scale. Straight lines show conformity.

Fig. 9 shows such a test for conformity to Beer's law for the iron-phenanthroline curves of Fig. 8. Readings were taken at 508 $m\mu$, the wavelength of minimum transmittance.

Non-conformity to Beer's law may be attributed (1) to insufficient refinement of the instrument, most likely a spectral band width too wide, or (2) to some change in the nature of the absorbing species with dilution.

Analytical Determinations. The nature of quantitative applications may be considered in terms of the number of constituents to be measured in a sample.

(a) *One Constituent.* In general, two techniques are used to determine single constituents. In the first technique a series of solutions is measured in order to establish a calibration curve. Usually the wavelength of measurement is that of minimum transmittance (maximum absorbance), such as 508 $m\mu$ in Fig. 8. The cell thickness should be that to be used for unknowns, and the

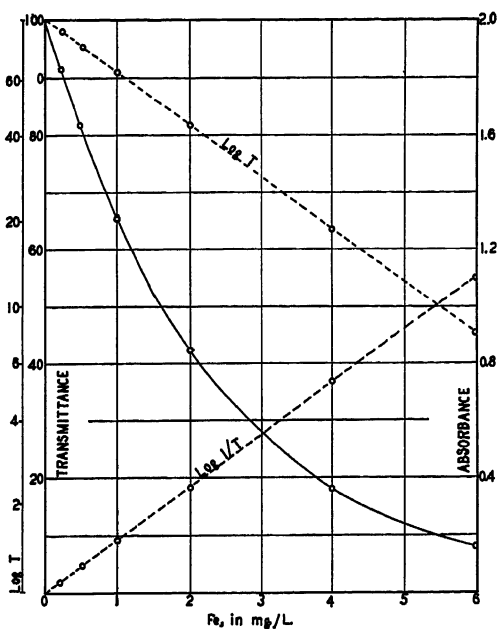


FIG. 9. Transmittance and Beer's law curves for iron-phenanthroline solutions.

range of concentrations should be suitable for the absorptive capacity of the system concerned. In Fig. 8 this range is 0.5 to 4 mg./liter. Having made the transmittance (absorbance) measurements, a calibration curve such as one of those in Fig. 9, is plotted. Application of the method then involves only the determination of the photometric reading for the unknown, location of this value on the curve, and reading the amount of desired constituent on the abscissa scale. It should be emphasized that each laboratory should establish its own calibration curve with its particular instrument used in the recommended way.

A less common type of calibration curve was proposed by Ringbom. Per cent transmittance or absorbance is plotted on a linear scale and concentration on a log scale. Fig. 10 illustrates such curves for the solutions of Fig. 8. Measurement should be restricted to the reasonably straight portions of the curves, that is, the concentration range of 0.5 to 4 mg./liter.

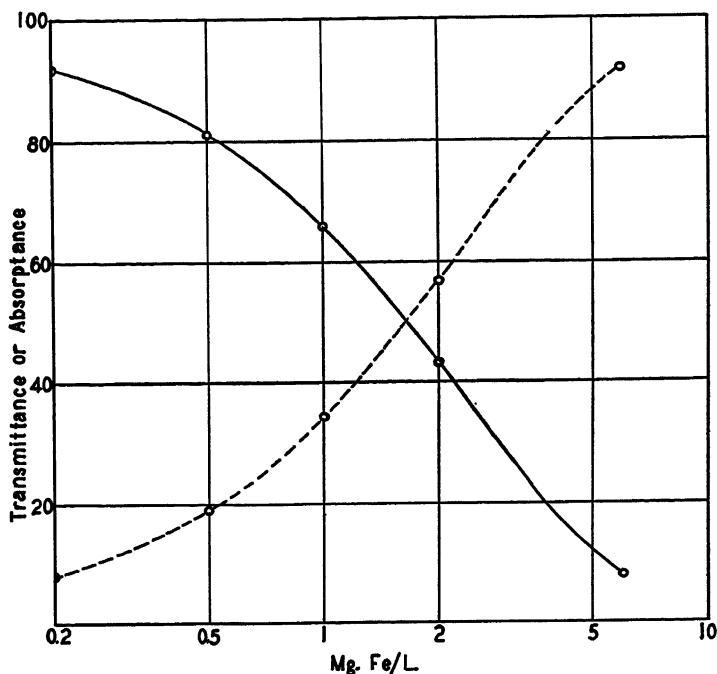


FIG. 10. Ringbom calibration curves for iron-phenanthroline solutions.

In the second technique application of the Bouguer-Beer equation in the form

$$c = A/ab$$

is made. The value for b is known and A is measured (or calculated from P/P_0). Knowing the specific or molar absorptive constant, a , the concentration c may be calculated. The unit for c will be that used in determining a .

Unfortunately, the practice of spectrophotometry has not been sufficiently refined to make possible the compilation of a generally usable table of absorbance indexes. Ideally, these should be constants comparable in reliability to refractive indexes and densities. It was noted in connection with Fig. 6 that the value of the transmittance at about 530 $m\mu$ is very greatly influenced by the spectral band width. Consequently, the calculated absorbance index will vary accordingly. It would seem, therefore, that generally usable constants cannot be expected until we have instruments operating on a

band width sufficiently narrow that any narrower band will not affect the constant significantly. This situation is such in infrared work that there is practically no mention in publications of molar absorbance indexes.

In addition to the effect of band width upon the absorbance index, the chemical preparation of the system for measurement, if any, and the general technique of making the measurement may have a significant effect upon the measured photometric value. With all these possibilities in mind, the experienced analyst will determine the constant with his instrument by the technique approved in his laboratory.

For decades it was almost traditional to state that absorptimetric methods in the visible region are limited to trace amounts of desired constituents. The most sensitive methods are in the neighborhood of 0.001 mg/liter. It has been shown that over 50 per cent iron can be determined with an accuracy approaching 0.1 per cent, by meticulous attention to operative details with

standard colorimetric methods. Much work with fairly high percentages is being done in the infrared region, but with nowhere near 0.1 per cent accuracy. A differential technique now provides for handling major components, such as 95 per cent copper in an alloy. It involves determining the photometric value by comparison with a standard of nearly the same composition as that of the unknown.

(b). *Two (or more) constituents.* Spectrophotometers capable of operating on narrow spectral band widths have their most distinctive value for systems containing two or more absorbing components.

In polycomponent systems three situations, more or less distinct, may arise. In the first situation the absorbance curves of two components are such that the absorbance for one of the desired constituents may be determined at a wavelength where the second constituent does not interfere (its absorbance is zero).

In the second situation the readings have to be made at a wavelength where both constituents absorb, but it is possible to correct for the effect of one of them by means of readings at a different wavelength. To make such a correction readily it is very desirable to have the absorbances additive, that is, each of the two components should conform to Beer's law.

In the third situation the curves for the constituents of the mixture are such that the preceding possibilities are inapplicable. In general, solution of this problem depends upon using equations involving absorbances of each component and of the mixture at suitably selected wavelengths.

The determination of α and β -chlorophylls in mixtures of the two illustrates this type of application. Fig. 11 shows the absorption spectra of the pure chlorophylls plotted in terms of specific absorbance index a .

In considering solutions in which two (or more) components absorb at the wavelengths employed, the values of A and of abc for the

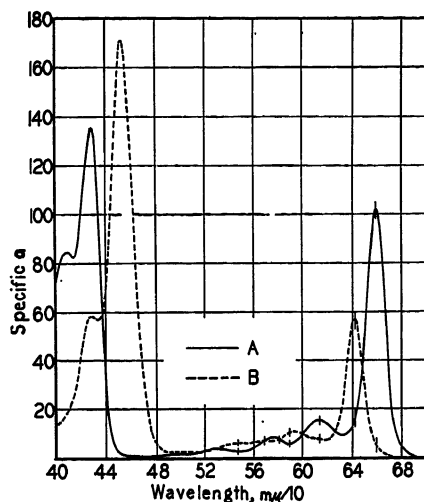


FIG. 11. Absorption spectra of chlorophylls A and B.

individual components are additive. The absorbance index, a , is an intensive property and is not additive. Thus, for a given wavelength

$$A \text{ (observed)} = A_1 + A_2 = a_1 b_1 c_1 + a_2 b_2 c_2$$

Values for the concentration of each of n components may be obtained from absorbance measurements at n wavelengths, where no two curves coincide or intersect; however, no two wavelengths may be used at which absorbances for two components have the same ratio. This is the general case.

For the two-component system of the chlorophylls, where b is constant, the equations are simplified to

$$A = (a_1' c_1 + a_2' c_2) b$$

and

$$A = (a_1'' c_1 + a_2'' c_2) b$$

where A = measured value at the given wavelengths; a_1' and a_2' = the specific absorbance indexes of components 1 and 2, respectively, at wavelength λ' ; a_1'' and a_2'' = the specific absorbance indexes of components 1 and 2, respectively, at wavelength λ'' ; and c_1 and c_2 = the concentrations of components 1 and 2, respectively, in grams per

liter. These two equations may be solved simultaneously for the two unknowns, c_1 and c_2 .

The total concentration C , in grams per liter, can be obtained by determination of A at a coincident point of the two curves. Then the general equation reduces to

$$A = abC$$

in which $C = c_1 + c_2$. If the total concentration is known, the composition may be determined by measurement of the absorbance at one suitable non-coincident point. Such a solution would involve use of the equation just given, along with the general one given first.

Maximum analytical accuracy is achieved when the relative heights of the curves at the two wavelengths are reversed for the two components. Inaccuracies are easily introduced when readings are taken on steep slopes. In general, the accuracy is improved with increase in the distance between the two curves at the wavelength employed. Thus, at wavelengths 546 and 589 $m\mu$ the analytical results are very sensitive to light-absorbing impurities.

In the determination of chlorophylls, based on the curves of Fig. 11, absorbances may be made at the following wavelengths: 642 and 660 $m\mu$ for total chlorophyll and for percentage composition; 568, 581, and 600 $m\mu$ for checks on total chlorophyll; and 546, 589, and 613 $m\mu$ for checks on percentage composition.

The example cited is a simple case of applying this type of indirect method of chemical analysis. However, it does illustrate the general principle. Slowly the method has been extended to polycomponent systems of more and more desired constituents. The major deterrent to more extensive application is that in many cases the absorption spectra of the individual components are not suitably related to each other to make satisfactory results possible. Also, as is generally true with indirect determinations, the reli-

ability of results is not all that one might desire, even with the most carefully measured absorbances. Where such methods are applied to mixtures, however, there is usually no satisfactory alternative. A good example is the infrared determination of *cis-trans* isomers in a mixture of the two. Electrical computers facilitate the calculations.

Color analysis. In the visible region of the spectrum spectrophotometers have a unique application. Absorption spectra, in the form of curves, provide the fundamental basis for specifying a color in terms of the radiant energy evoking the sensation. With the reflectance or transmittance curve for a substance, one can then calculate a numerical colorimetric specification for the substance in terms of equivalent stimuli.

REFERENCES

1. BERL, W. G. (ed.), "Physical Measurements in Chemical Analysis," Vol. I. Academic Press, New York, 1950.
2. BOLTZ, D. F., "Selected Topics in Modern Instrumental Analysis," Chap. 4. Prentice-Hall, New York, 1952.
3. GILLAM, A. E., STERN, E. S., AND JONES, E. R. H., "An Introduction to Electronic Absorption Spectroscopy," Ed. Arnold (Publishers), London, 1954.
4. LOTHIAN, G. F., "Absorption Spectrophotometry," Hilger and Watts, London, 1958.
5. MELLON, M. G. (ed.), "Analytical Absorption Spectroscopy," J. Wiley & Sons, New York, 1950.
6. MULLER, E., "Methoden der Organische Chemie," III, pp. 593-765; 795-917, G. Thieme Verlag, Stuttgart, 1955.
7. WEST, W. (ed.), "Chemical Applications of Spectroscopy," Interscience Publishers, New York, 1956.

M. G. MELLON

ATOMIC ABSORPTION SPECTROCHEMICAL ANALYSIS

In recent years a new absorption spectrochemical method for determination of certain elements in laboratory samples has attracted great interest. The sample is con-

verted into an atomic vapor so that the sought-for elements in the vapor exist mostly (and preferably) as neutral atoms in the ground state. In this state each specific element in the atomic vapor absorbs its characteristic monochromatic resonance radiation. Therefore, under controlled conditions the measured absorption of a characteristic wave length can indicate the presence and quantity of a specific element in a sample. The inherent high selectivity and simplicity, and the possibilities of quantitative methods with high sensitivity and exceptional accuracy at low concentrations are the attractive analytical features.

In general the basic requirements for *atomic absorption spectrochemical analysis* can be represented by the block diagram (Figure 1). Monochromatic sources, such as hollow-cathode discharge tubes or Wotan lamps which produce resonance lines for each sought-for element, are set up and the radiation passed through the atomic vapor. The selected wave lengths are then either sequentially isolated (by a prism, grating or filter) and passed onto a single radiation transducer or simultaneously isolated with separate filters with each wave length inci-

dent on a separate transducer. The transducer converts the incident radiation of each specific wave length into an electrical signal (current or voltage) related to the intensity. At a selected wave length, electrical signals are often obtained with and without sample vapor in the cell. These signals can be compared by the measurement system to provide an absorbance value related to the concentration of a specific element in the vapor. However, this measurement has little meaning unless the relationship between the concentration of absorbing neutral atoms for the sought-for element in the atomic vapor and the concentration of the element in the original analytical sample is carefully controlled. Ideally there should be a direct proportionality between the two under a given set of conditions which are readily maintained. Also, it would be desirable to determine elements in all types of sample solutions or solids.

The practical development of the method hinges largely on the success of various experimental techniques to form atomic vapors reproducibly from particular analytical samples. Suitable atomic vapors from solution samples have been reproducibly formed by

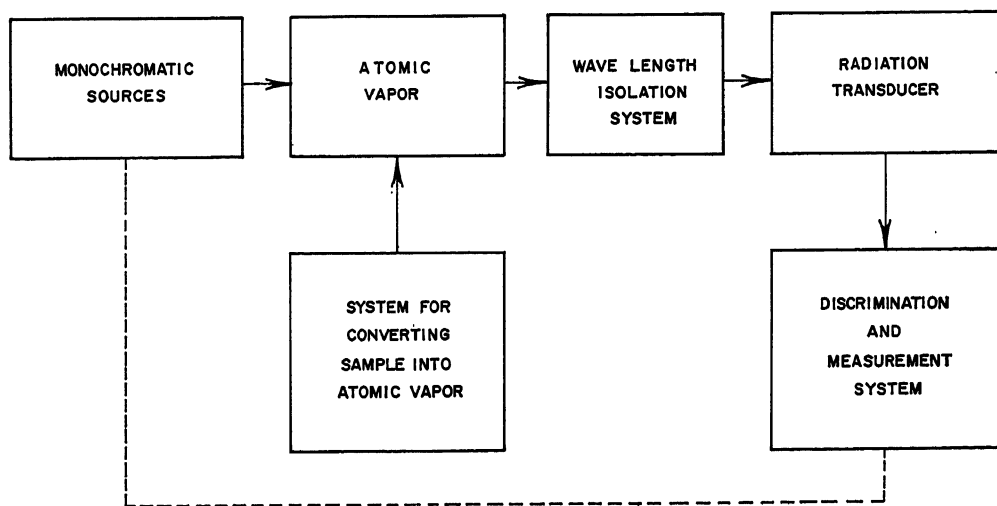


Fig. 1. Block diagram showing basic requirements for atomic absorption spectrochemical analysis.

atomizer-combustion systems similar to those used for flame emission spectrochemical analysis. Techniques for providing suitable atomic vapors directly from various solid samples will undoubtedly be developed in the future.

In the process of forming the atomic vapor a significant fraction of the atoms might be excited with subsequent emission of radiation. If the emitted radiation is the same wave length as that from the source it must be discriminated against in measuring the absorption. In Figure 1 the dotted line indicates that the discrimination is often associated with both the source and measuring system. The source can be modulated with a chopper and an AC amplifier employed in the measuring system so that only the intensity of radiation from the source is indicated. A wave length isolation device would not be necessary when using a single source for a single absorbing constituent and suitable discrimination against emitted radiation.

If an absorption cell is used its design depends on the type of sample and associated system for obtaining the atomic vapor. The cell must obviously have a path transparent to the selected wave lengths.

Although the atomic absorption method has only recently been recognized as a rather general quantitative tool, the basic principles have been known for many years. It has been used for determining the composition of solar and stellar atmospheres,^{5,7} the measurement of flame temperature,² and the specific determination of mercury in various samples.^{1,3} Also, self-absorption of emitted radiation has been recognized as a source of errors in quantitative emission spectrochemical analysis.

In 1955 Walsh⁸ focused attention on the comparison of atomic absorption to flame emission spectrochemical methods and showed that there are fundamental reasons favoring the absorption over the emission method. The factors governing the relationship between atomic absorption and the

concentration of sought-for element in the atomic vapor indicated that the absorption method should be less susceptible to temperature effects, and the sensitivity should be greater for elements such as zinc and cadmium which are excited with difficulty. This comparison between emission and absorption methods stimulated much interest in the analytical possibilities by the atomic absorption spectrochemical procedure.

Walsh and co-workers have described an atomic absorption spectrophotometer,⁶ and the method has been applied by others for the determination of Ca, Mg, Zn, Fe, Mn, Ag, Au, Pt, Pd, Rh, Cu, Na and K.

Basic Considerations of Atomic Absorption for Solution Samples. The present development of the atomic absorption method is with solution samples for which an atomizer-combustion system produces the atomic vapor. Therefore, it is worthwhile to consider a general relationship between the concentration of a sought-for element in a solution and the observed meter reading for a typical system. Such a relationship points out the variables that must be controlled for quantitative analysis. An analysis of the variables indicates why atomic absorption should be less susceptible to certain errors than emission methods and also its limitations.

It is assumed that solution sample *S* contains a certain sought-for element *M*, at an unknown concentration C_{MS} . A portion of this solution is atomized to form a fine mist. The total number of atoms of element *M* sprayed from the atomizer per second, $(N_{MS})_{\text{spray}}$, is given by equation 1:

$$(N_{MS})_{\text{spray}} = N F C_{MS} \quad (\text{Eq. 1})$$

where *N* is Avogadro's number and *F* is the flow rate of solution through the atomizer. The flow rate *F* depends on the radius and length of capillary, solution physical properties such as viscosity and surface tension, pressure of the aspirating gas, and hydrostatic head of solution on the atomizer tip.

It is also assumed that the fine mist passes through a heated chamber where a fraction, f_1 , of the spray is desolvated and then passed into the flame as small salt crystals. The number of atoms of element M in the salt crystals entering the flame per second, $(N_{MS})_{salt}$, is expressed in equation 2:

$$(N_{MS})_{salt} = f_1(N_{MS})_{spray} \quad (\text{Eq. 2})$$

The factor f_1 takes into account the portion of atoms of element M which are sprayed from the atomizer but do not become desolvated or enter the flame. It depends on the type of atomizer used, the size and distribution of spray droplets, the relationship between atomizer capillary and atomizing gas stream, the shape and temperature of heated chamber and the physical properties of the solution.

A fraction, f_2 , of the desolvated salt crystals is decomposed in the flame to provide a vapor which contains element M, primarily as neutral atoms but also in other forms. The number of atoms of element M passing through the vaporization zone per second, $(N_{MS})_{vapor}$, is given by equation 3:

$$(N_{MS})_{vapor} = f_2(N_{MS})_{salt} \quad (\text{Eq. 3})$$

The factor f_2 takes into consideration the particles of salt that exist in the cooler portion of the flame and are not vaporized. It depends on the flame temperature and crystal energy of the salt.

A fraction, f_3 , of the atoms of element M exists in the vapor as neutral atoms and the number passing through the vaporization zone per second, $(N_{MS})_n$, is given by equation 4:

$$(N_{MS})_n = f_3(N_{MS})_{vapor} \quad (\text{Eq. 4})$$

The factor f_3 takes into consideration that some atoms of element M might be ionized or react to form gaseous compounds (such as oxides) and depends on the ionization potential of element M, the stability constants of possible gaseous compounds, and the flame temperature. The most serious limitation

for the general application of the atomic absorption method is that several elements, such as Si and Al, exist primarily as molecular species in the usual flames. However, higher temperature combustion systems might eliminate this problem.

A fraction, f_4 , of the neutral atoms is capable of absorbing a resonance line of wave length, λ_1 , characteristic of element M. The total number passing through the vaporization zone per second, $(N_{MS})_n^{\lambda_1}$, is given by equation 5:

$$(N_{MS})_n^{\lambda_1} = f_4(N_{MS})_n \quad (\text{Eq. 5})$$

The factor f_4 takes into consideration that some of the neutral atoms are excited to higher energy levels in the flame and are not in the necessary ground state to absorb, and also that there is an energy distribution of neutral atoms in the ground state. The value of f_4 depends on pressure broadening either by atoms of the same kind or by foreign gases and the excitation energy of the flame.

The radiant power of wave length λ_1 from the source which is transmitted through a fixed segment of the vapor column depends on the number of absorbing atoms in the light path. If the radiant power transmitted is P_0 when the solvent is sprayed and P_s for a sample solution producing absorbing atoms of element M, then from the absorption law the absorbance, A_s , is:

$$A_s = \ln \frac{P_0}{P_s} = q(N_{MS})_n^{\lambda_1} \quad (\text{Eq. 6})$$

where q is the absorption coefficient characteristic of the specific element M. It is assumed that the half-width of radiation from the source is less than the half-width of the absorption band, and that no absorbing species other than the neutral atoms of element M are formed from the sample solution which are different than those from the solvent.

It is assumed that the radiation detector provides an output voltage directly proportional to the radiant power, and the output

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voltages are E_0 and E_s when the radiant powers are P_0 and P_s , respectively. Combining equations 1 through 6 gives:

$$A_s = \ln \frac{E_0}{E_s} = qf_1f_2f_3f_4NFC_{MS} \quad (\text{Eq. 7})$$

If A_s is the value read from the measuring system it can be seen from equation 7 that there are many variables which must be maintained constant or compensated to have a direct proportionality or reliable relationship between A_s and C_{MS} .

One experimental technique for increasing precision and accuracy is by a null-point system which eliminates difficulties from some of the above variables.⁴

The Precision Null-Point Method. The principle of the null method is simple. The concentration of a sought-for element is continuously varied in a reference solution, by adding reagent from a buret, until it is equal to the concentration of the same element in the unknown solution. The concentration of the reference, and therefore the unknown, is readily calculated from the amount of element added in a known total volume. The instrument operates as a specific null detector for each element, by forming the atomic vapors and measuring the absorption of characteristic monochromatic radiation for both variable reference and unknown solutions under nearly identical conditions.

If a reference solution R containing element M is atomized and vaporized and the absorbance measured with the same system as above then it follows from the development of equation 7 that,

$$A_s' = \ln \frac{E_0'}{E_R} = qf_1'f_2'f_3'f_4'NF'C_{MR} \quad (\text{Eq. 8})$$

where the terms have the same significance as in equation 7, but for a reference solution whose concentration, C_{MR} , is always known.

If C_{MR} is continuously varied until $E_R = E_s$, and if the detector response is constant, and the source of monochromatic radiation

is constant so that $E_0 = E_0'$, then equations 7 and 8 can be combined to give

$$C_{MS} = \frac{f_1'f_2'f_3'f_4'F'}{f_1f_2f_3f_4F} C_{MR} \quad (\text{Eq. 9})$$

A null-point instrument can be constructed so that the final comparison between reference and unknown can be performed within a few seconds using the same atomization-vaporization system for both. Therefore, the atomization, vaporization, and measurement conditions are nearly identical, and $(f_1'f_2'f_3'f_4'F')$ is essentially equal to $(f_1f_2f_3f_4F)$; and it follows that,

$$C_{MS} = C_{MR} \quad (\text{Eq. 10})$$

The precision of determining the unknown concentration depends on the precision of the instrument in establishing the null point (the meter indication that the concentrations

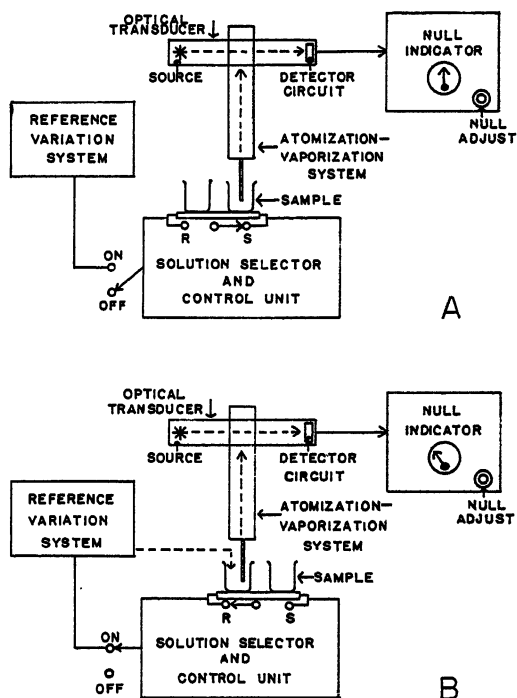


FIG. 2. Basic sections of the precision null-point atomic absorptionmeter.

A. Sample position.

B. Reference position.

ATOMIC ABSORPTION SPECTROCHEMICAL ANALYSIS

of sought-for element in both reference and unknown are apparently the same) and the precision of the volumetric apparatus used to vary C_{MR} . The accuracy depends on whether conditions are selected so that the

factors do not change in switching from sample to reference.

The null-point system enables exceptional precision, accuracy, sensitivity, and selectivity to be obtained for certain elements

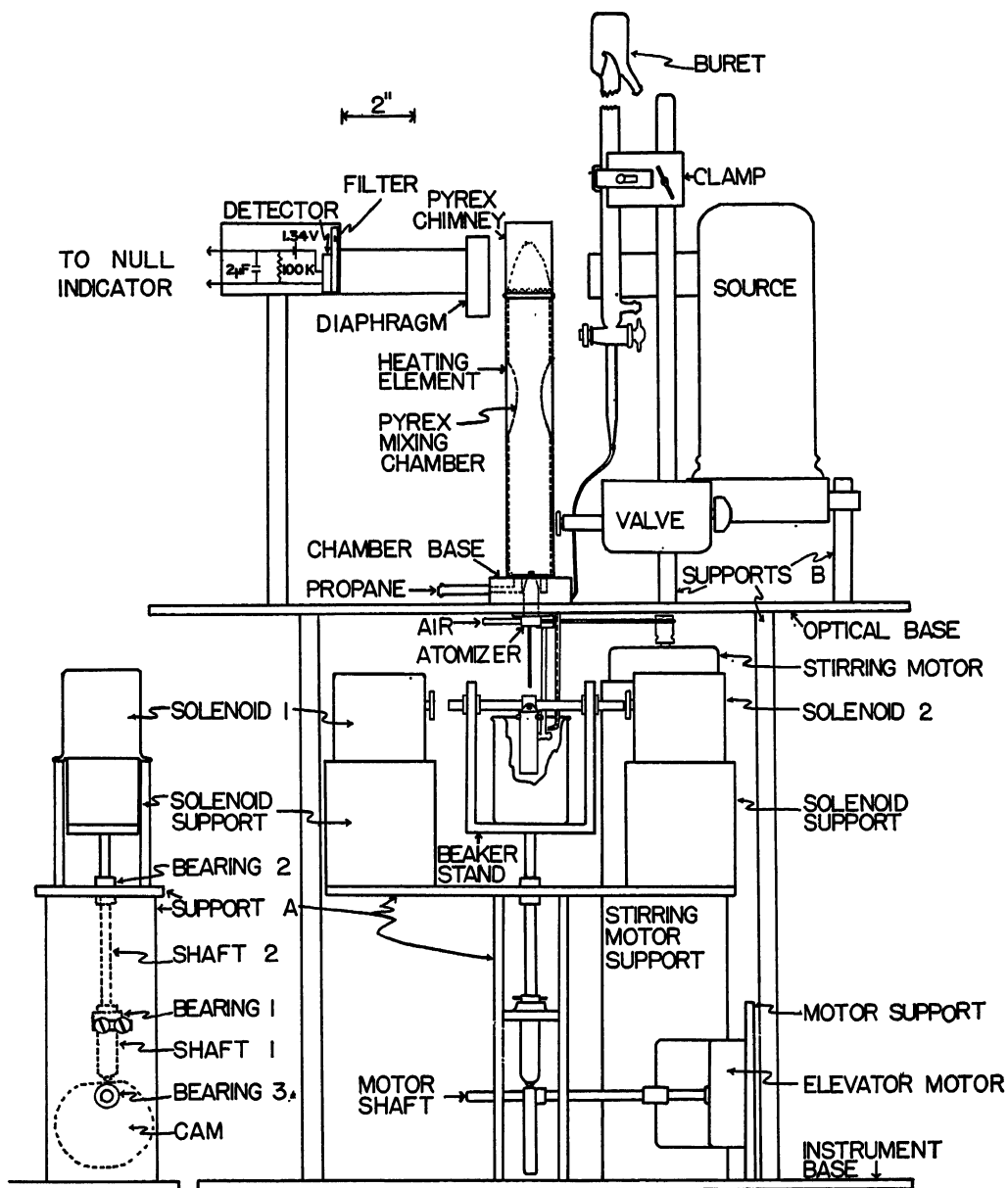


FIG. 3. Integrated sections of the null-point absorptiometer. (Solutions are shown in the "Down" position).

with a low-cost instrument, compensates for changes of the atomization-vaporization system and measurement device (thereby greatly simplifying the instrument design), provides self-standardization for each sample, and eliminates the need for linear response characteristics or working curves.

The basic sections for a null instrument are illustrated in Figure 2. When the solution selector is in position S (Figure 2A), the atomization-vaporization system converts a small volume of unknown sample into an atomic vapor which contains the atoms of the sought-for element mostly in the ground state. The vertical dotted arrow indicates that the atomic vapor, formed continuously from the solution, moves rapidly through the light path of an integrated optical transducer (consisting of monochromatic source, filter and radiation detector). Each transducer is specific for a particular element and provides an output voltage related to the number of atoms of sought-for element in the light path per unit time. The output voltage, also related to the concentration of a specific element in the unknown solution, is fed to the null indicator unit. The "Null Adjust" control provides an opposing voltage equal to the transducer output voltage so that zero (0) on the meter becomes the null point.

After adjusting to a zero (0) meter reading with unknown in position, the solution selector is thrown to position R (Figure 2B) to reverse position of the solutions so that the variable reference is atomized instead of unknown. The variable reference system now provides a continuously variable reference solution concentration of sought-for element until the meter reads 0 again. This indicates that the concentration of unknown is equal to the concentration of the reference at the null point, assuming that atomization, vaporization, optical transducer, and null

indication systems remain constant between adjusting the 0 point with the unknown sample (position S) and re-establishing the 0 point by varying the reference concentration (position R). The time for this complete operation varies, but it is often about $\frac{1}{2}$ to 2 minutes. Therefore, it is desirable to check for a true null point over a few seconds by reversing between variable reference and unknown. If there are any differences, the concentration of the variable reference is changed again so that the transducer output voltages are equal when the rapid solution alternation is made, as indicated by the same meter reading.

A specific null-point atomic absorptiometer⁴ developed for sodium and potassium determinations at solution concentrations of 1 to 100 ppm is shown in Figure 3. Results with this instrument were excellent. For sodium the coefficient of variation was less than 0.2 % in some cases and about 0.5 % in most cases. Results for potassium were nearly as good. The accuracy was excellent because of the inherent selectivity and relative freedom from interelement effects.

REFERENCES

1. BALLARD, A. E., AND THORNTON, C. W. D., *Ind. Eng. Chem. (Anal. Ed.)*, **13**, 893 (1941).
2. GAYDON, A. G., AND WOLFPHARD, H. G., "Flames, Their Structure, Radiation and Temperature," Chapman & Hall, Ltd., London (1953).
3. LINDSTRÖM, O., *Anal. Chem.*, **31**, 461 (1959).
4. MALMSTADT, H. V. AND CHAMBERS, W. E., *Anal. Chem.*, **32**, (Feb. 1960).
5. ROSSELAND, S., "Theoretical Astrophysics," Clarendon Press, Oxford, (1936).
6. RUSSELL, B. J., SHELTON, J. P., AND WALSH, A., *Spectrochimica Acta*, **8**, 317 (1957).
7. UNSÖLD, A., "Physik der Sernatmosphären," chapters 11 and 13, 2nd edition, Springer-Verlag, Berlin, (1955).
8. WALSH, A., *Spectrochimica Acta*, **7**, 108 (1955).

H. V. MALMSTADT

CARY RECORDING SPECTROPHOTOMETRY.

See ANALYTICAL ABSORPTION SPECTROMETRY, p. 1.

COPPER MICRODETERMINATION

Copper forms a highly colored complex with the dihydrazone formed from oxalyldihydrazide and acetaldehyde in the presence of ammonia. The intensity of the color, which is measured spectrophotometrically, is linearly proportional to the copper concentration within the range specified below.

Procedure: Pipet the following into 10-ml volumetric flasks, in the order given:

1. Unknown or standard copper solution, to contain a total of approximately 2 to 10 micrograms of copper.

2. 1.2 ml of concentrated ammonia.

3. 0.8 ml of saturated oxalyldihydrazide solution.

4. 2.0 ml of cold 40 % acetaldehyde solution. Wait 15 to 20 minutes.

5. Copper-free water to volume.

Prepare a blank, using all reagents except the copper solution. Then:

(1) Wait at least 30 minutes from time of addition of acetaldehyde.

(2) Place reagent blank in one colorimeter cell (cylindrical, 3 ml volume, path length about 1 cm) and copper solutions in turn in second cell.

(3) Read coppers vs. reagent blank in colorimeter (Lumetron 402E was used by authors—Photovolt Corp., 95 Madison Ave., New York, N. Y.) with a narrow-band filter, maximum transmittance about 550 m μ .

(4) Calculate concentration of unknown from the change in optical density per microgram of copper, previously calculated from the absorbance of the standards.

Notes:

(1) Use copper-free water throughout. For preparation, see reference 1.

(2) For synthesis of oxalyldihydrazide, see reference 3.

(3) A standard copper solution (about 25 micrograms per ml) is conveniently pre-

pared by dissolving a weighed piece of electrolytic copper in redistilled concentrated nitric acid and diluting to volume with copper-free water.

(4) Color is constant and maximum for at least 48 hours in the pH range 8.2 to 10.1.

(5) Volumes of reagents other than copper need not be measured with great precision.

(6) The method is accurate to ± 2 or 3 %.

(7) For further details, see reference 1.

REFERENCES

1. STARK, G. R. AND DAWSON, C. R., *Anal. Chem.*, **30**, 191 (1958).
2. AMES, S. R., AND DAWSON, C. R., *Ind. Eng. Chem. (Anal. Ed.)*, **17**, 249 (1945).
3. GRAN, G., *Anal. Chim. Acta*, **14**, 150 (1956).

G. R. STARK AND C. R. DAWSON

DIFFERENTIAL SPECTROPHOTOMETRY*

Introduction. Spectrophotometric methods of analysis are characteristically rapid, sensitive, and selective. These features make spectrophotometric methods extremely useful for the rapid analysis of complex mixtures and for the determination of trace constituents in a sample. Because a high degree of accuracy is not usually required in this type of work, many analysts have concluded that spectrophotometric methods are inherently inaccurate and are of little use in the analysis of major constituents where accuracy corresponding to a relative error of one or two parts per thousand or less is desired.

As early as 1937, however, Kortüm²⁰ had reported the determination of the concentration of a 2,4-dinitrophenolate solution with a relative error of only 0.02 per cent using a sensitive spectrophotometer of his own design. Bastian⁶ in 1949 showed how a typical modern spectrophotometer could be used for the determination of large amounts of copper with a relative error of only one to three parts per thousand. Numerous papers

* Contribution No. 817. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

on differential spectrophotometry,^{2, 3, 4, 5, 12, 23, 25, 34, 35} differential colorimetry,⁹ differential absorptiometry,¹⁴ precision spectrophotometry,¹ precision absorptiometry,¹¹ and precision colorimetry^{15, 29, 33} have since appeared in the literature which discuss the theory and (or) give applications of methods designed to reduce the relative error in spectrophotometric concentration measurements. The above list of references is by no means exhaustive and includes only papers concerned with the precise determination of the concentration of a sample from spectrophotometric measurements. The multiplicity of names and, even more seriously, an apparent confusion in the use of terms like accuracy and precision make an intelligent appraisal of the usefulness of the various spectrophotometric "methods" which have been proposed somewhat difficult.

The term, differential spectrophotometry, will be used by the authors to refer to that spectrophotometric technique in which the concentration of an unknown sample is determined by measuring its transmittance or absorbance relative to a reference sample of known concentration for the specific purpose of reducing the relative concentration error. In the following discussion, it will be assumed that the sample is in the form of a solution and the spectrophotometric measurements are made in the ultraviolet or visible region of the spectrum. This is usually the case when the purpose of the spectrophotometric measurements is the determination of concentration.

The specific purpose of differential spectrophotometric methods then is to decrease the *relative concentration error*. Error is a measure of the accuracy of a measurement, i.e., the difference between the measured value and the true value, but this *absolute error* is of no practical importance. Accuracy necessitates precision, so a secondary purpose of differential spectrophotometric methods is precision, i.e., the reproducibility of a measurement. The standard deviation, σ , is

a measure of the precision of a method and again the quantity of practical importance is the value of σ relative to the arithmetical mean of the measurements. This relation is often expressed in parts per thousand and is a measure of the relative precision of a measurement. Qualitatively high precision is associated with a small value for the standard deviation, σ , so precision is more conveniently expressed as the reciprocal of the standard deviation and the relative precision as the product of this quantity and the arithmetical mean.

Some confusion concerning the significance of precision in differential spectrophotometry is evident in the literature. The confusion is apparently caused by the failure on the part of some authors to distinguish between relative and absolute precision and to distinguish between the precision with which spectrophotometric measurements are made and the precision of the desired concentration measurements.

An analogy can be made with the use of the analytical balance which helps to clarify the distinction between accuracy and precision and also the advantages of a relative measurement. Suppose an object of such a mass is placed on one pan of a balance that the pointer does not swing off scale when the beam is released. The mass of the object can be calculated from the deflection of the pointer and some previously determined relation between the magnitude of the deflection and the mass. The precision with which the mass of the object can be determined is then directly proportional to the precision with which the magnitude of the deflection can be measured. Note that if the absolute uncertainty in measuring the magnitude of the deflection is constant over the entire scale, the relative precision increases as the magnitude of the deflection increases. It is quite obvious in the case of the balance, however, that the relative precision of mass measurements is not limited by the precision with which the deflection of the pointer can

be measured. An object of mass so great that it could not be determined by the deflection method can be determined by comparison with a standard mass. In this case, even though the precision with which the deflection of the pointer can be measured is no better, and possibly not as good, the *relative precision* with which the mass of the unknown can be determined can be very much greater. It should be noted that the *relative error* in the determination of the mass of the object depends on the accuracy with which the mass of the standard is known, the medium in which the masses are compared, and other factors as well as the precision with which the deflection of the pointer can be measured.

If the purpose of a spectrophotometric measurement is the measurement of the concentration of a solution, it seems an obvious extension of the above ideas to determine the concentration of an unknown solution by measuring its absorbance or transmittance relative to some reference solution of known concentration. The manner in which this can be accomplished and its effect on the relative error in the final concentration measurement are the subject matter of this discussion.

The use of a differential method can decrease the relative error in the final concentration measurement in two ways. Analogous to the comparison of masses with an analytical balance, the determination of the concentration of an unknown sample by measuring its transmittance relative to a reference sample of known concentration can result in an increase in the relative precision of the concentration measurement. This is because any error in the spectrophotometric measurement in this case only results in an error in the difference in concentration between the sample and reference solutions. A second way in which the use of a differential method may reduce the relative error is in the compensation of systematic errors due to the use of a relative measurement. The impor-

ance of this feature can hardly be over-emphasized.

An example in which the compensation of systematic errors due to the use of a differential method or measurement is very advantageous is the spectrophotometric analysis of lanthanon mixtures. The extremely narrow absorption bands of the lanthanons in aqueous solution makes the spectral position used extremely critical if the concentration is to be determined from a measured absorbance value and the absorptivity of the particular lanthanon at a given spectral position. If the concentration is determined by a differential method, a slight error in spectral position will affect both the reference and sample absorbances, and in the optimum case, where the concentrations of reference and sample are the same, the errors would exactly compensate.

The compensation of errors which results from the use of the differential method makes this method generally useful even for trace analysis. The maximum increase in precision possible with a differential method will probably not be realized in this case if the sample size is limited, but the advantages of using a relative method may still be appreciable. The application of the differential method to indirect spectrophotometry has also been reported^{23, 24, 30} to result in an increase in precision. The use of an indirect method actually has a unique advantage in the precise measurement of concentration. The use of indirect and indirect-differential methods for this purpose are considered.

The objective of this report is to review the principles underlying differential spectrophotometry and to evaluate and relate the usefulness of the various "methods" which have been proposed. An attempt will be made to follow the nomenclature suggested by the Joint Committee on Nomenclature in Applied Spectroscopy¹⁹ or that used by Gibson¹³ in cases where the former report makes no suggestion. To avoid confusion, absorbance or transmittance values

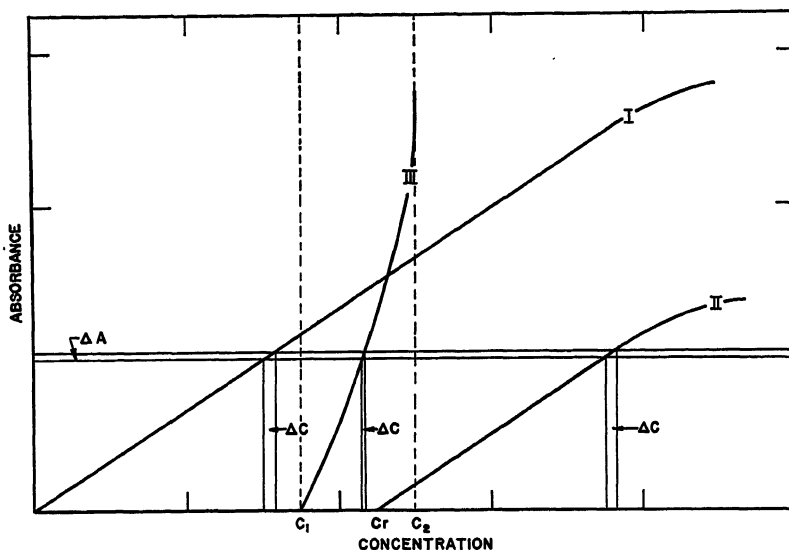


FIG. 1. Absorbance-concentration relationships. a) Curve I—Ordinary method. b) Curve II—Transmittance-ratio method. c) Curve III—Two-reference method.

relative to some reference other than solvent will be primed.

Principles of Differential Spectrophotometry. If the absorbance of a sample is related to its concentration in some manner such as is illustrated by curve I in Figure 1, the equation relating the relative uncertainty in concentration, $\Delta C/C$, to the uncertainty in absorbance, ΔA , is given by

$$\Delta C/C = \Delta A/SC \quad (1)$$

where S is the slope of the absorbance-concentration curve at any concentration, C .^{9, 18, 22} Equation 1 is independent of Beer's law which is a special case when S is constant. The conditions necessary for high precision or low relative error in the measurement of concentration insofar as the spectrophotometric measurements are concerned are obtained when ΔA is as small as possible and the product SC is as large as possible. Spectrophotometric methods have been proposed which attempt to reduce the relative error by decreasing ΔA , by increasing C , and by increasing S .

The magnitude of the uncertainty in the measurement of the absorbance, ΔA , has an

optimum value characteristic of the particular instrument used. With modern photoelectric spectrophotometers, the absorbance measurement can probably be reproduced to within 0.001 to 0.003 absorbance unit near the zero end of the absorbance scales.¹⁰ Instruments have been designed, however, with much greater sensitivity. Kortüm²⁰ summarizes much of the early work in the field of instrument design and describes an instrument of his own design based on the optical null principle and employing two phototubes. With this instrument, Kortüm was able to determine the absorbance of a solution of 2,4-dinitrophenolate having an absorbance of 0.34235 with a deviation from the mean on five separate measurements of only $\pm .000014$ absorbance unit.

The papers by Kortüm²⁰ and Kortüm and Seiler²¹ are highly recommended for anyone interested in precision spectrophotometry. These authors discuss the basic principles underlying spectrophotometric instrumentation and measuring techniques and carefully distinguish between terms like sensitivity and reproducibility as opposed to accuracy which are so often confused in the literature.

Relative and "absolute" measurements are also discussed and the reason that concentration measurements can be made with much greater precision than can "absolute" molar absorptivity measurements is explained. In a series of experiments in which the concentration of an unknown solution was determined over a period of two days by comparative measurements with a solution of similar absorbance, Kortüm²⁰ showed that, although the "absolute" value of the absorptivity varied within 0.5%, the precision of the concentration measurements was within 0.02%. Apparently, those factors which caused the absorptivity to vary with time affected the reference solution and unknown solution to the same extent. This type of compensation is most complete when the concentration of the unknown and reference solution is identical.

The work of Kortüm²⁰ very clearly illustrates the danger in assuming that any increase in spectrophotometric precision necessarily results in an increase in the precision with which the concentration can be measured. The extreme sensitivity of his instrument coupled with the technique of comparative measurement of the sample with a reference of similar absorbance did result in a significant increase in the precision of concentration measurements, however.

The potential of this type of relative measurement was recognized by Bastian⁶ and Hiskey¹⁵ who respectively demonstrated the experimental feasibility of differential spectrophotometry and developed the theory underlying the method. Hiskey¹⁵ and Hiskey and co-workers^{16, 17, 18} and Bastian^{6, 7, 8} and Bastian and co-workers⁹ showed that the precision of concentration measurements could be greatly increased without special instrumentation. The increase in precision was accomplished by careful attention to the source of spectrophotometric error and by using the spectrophotometer in a rather special way as a "null point" indicator.

The following quotation from Bastian⁶

illustrates the theoretical gain in precision of the concentration measurement when a differential method is used.

"Assume that a concentration of 0.2 gram of copper per 100 ml. can be determined by the normal method with an accuracy of 1%. If the color obeys Beer's law at higher concentrations, a difference in concentration of 0.2 gram of copper per 100 ml. will always give the same difference in extinction.

"Yet if an attempt is made to take ten times the concentration of copper in the hope of getting ten times as much accuracy, the density reading will be off the scale; and even if such a high density could be read, the percentage error in making such a reading would be greater than the error in reading the lower concentration.

"This is all based on the assumption that the optical density scale is set for zero (or the transmittancy scale for 100%) using distilled water.

"Suppose, however, instead of using distilled water for this purpose, a solution containing 1.8 grams of copper per 100 ml. were used. A solution containing 2.0 grams of copper per 100 ml. read against this standard should then give the same scale reading that a concentration of 0.2 gram of copper per 100 ml. gives against distilled water.

"If it is possible to determine the 0.2-gram difference at the higher concentration to an accuracy of 1%, the total concentration is automatically determined to an accuracy of 0.1%. Such a process could be carried farther. If 19.8 grams of copper per 100 ml. were taken for the zero setting, and all the above conditions still applied, an accuracy of 0.01% could be obtained."

The limitation to this method, as recognized by Bastian, was in getting enough light through the highly absorbing reference solution so that the spectrophotometer could be balanced at zero absorbance. This was accomplished by using wider slit widths than normal and, consequently, less monochromatic light. This, of course, eventually re-

sults in an apparent departure from Beer's law. In terms of Equation 1, the slope, S , begins to decrease. The optimum conditions for a minimum value of $\Delta C/C$ are when the product SC is at a maximum. The relationship existing between the absorbance and the concentration in this method is shown graphically by curve II in Figure 1.

The usual employment of the spectrophotometer in which the transmittance of the sample relative to solvent is determined from the deflection on the instrument scale resulted in the development of a theory which predicted the "optimum" absorbance for the minimum relative concentration error.²¹ The confusion concerning the meaning to be attached to this theoretically derived "optimum" absorbance value makes it necessary to review its development and significance.

In absorption spectroscopy, the spectrophotometer is used to measure the ratio of the radiant power passing through a sample solution to the radiant power passing through a reference solution. If the reference solution is pure solvent, or a solution exactly similar to the sample solution but minus the constituent of interest, the ratio is referred to as the transmittancy of the sample.¹³ It is approximately equal to the ratio of the transmittance of the sample to the transmittance of the reference. Transmittance is defined as the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample, both measured at the same slit width and spectral position. The difference between the transmittancy and the ratio of the transmittances of the sample and solvent is due to a term involving the refractive index of the endplates of the cuvetts used which can usually be neglected if the refractive index of the endplate is less than 1.5.¹³ Strictly speaking, the scale reading obtained when a differential method is employed is neither the transmittance nor the transmittancy of the sample. Even in "ordinary" spectrophotometry the distinction between the two terms is not always

made. The spectrophotometer reading obtained on the linear scale is frequently referred to as the transmittance and the reading obtained on the logarithmic scale as the absorbance. This looser usage of the terms transmittance and absorbance has been followed in this discussion.

The phototube in a spectrophotometer responds in a fairly linear manner to the radiant power incident on its surface and hence to the transmittance of a sample. The response is amplified and indicated on a meter or scale which, if graduated in a linear manner, is referred to as the transmittance scale. A logarithmic scale may also be included which reads directly in absorbance because the absorbance, A , defined by

$$A = \log_{10} (1/T) \quad (2)$$

is usually approximately linear with concentration.

The relationship between the transmittance, T , the absorbance, A , and the concentration, C , of a sample is given by

$$C = \frac{1}{ab} \log_{10} (1/T) = \frac{A}{ab} \quad (3)$$

where a is the absorptivity and b the path length. Strictly, this is a limiting law for low concentrations and the constant, a , should be replaced by the expression $an/(n^2 + 2)^2$ where n is the refractive index²¹ of the sample. Because n is practically constant at low concentrations, it usually does not introduce a significant error to regard a as a constant, but in the case of differential spectrophotometry this might lead to a significant error.

If the spectrophotometer reading on the linear scale is assumed to be directly proportional to the transmittance, the relation between the scale reading and concentration is given by Equation 3. Now assume the uncertainty in reading the linear spectrophotometer scale is constant over the entire scale and is expressed as ΔT . If Equation 3 is differentiated with respect to T , finite incre-

ments substituted for the infinitesimals and the resulting expression divided by C and rearranged, the relationship

$$\frac{\Delta C}{C} = \frac{\Delta T}{T \ln T} \quad (4)$$

is obtained. The denominator $T \ln T$ reaches a maximum when $T = 0.368$. This corresponds to an absorbance of 0.434 on the logarithmic absorbance scale. A plot of T versus $1/T \ln T$ gives the knee-shaped curve familiar to most analytical chemists²¹ in which $1/T \ln T$ shows a broad minimum between $T = 0.20$ and $T = 0.65$ and becomes rapidly larger outside this range. If Beer's law is followed, Equation 4 shows that this transmittance range will also give the smallest relative error in concentration for a given error in transmittance. This is the reason for the statement in practically all analytical texts that the transmittance must be kept within the above limits for good precision.

It should be noted, however, that in the case of differential spectrophotometry, making the same assumptions that were made in the derivation of Equation 4, the concentration, C , is given by

$$C = \frac{1}{ab} \log_{10} 1/T' + \frac{1}{ab} \log_{10} 1/T, \quad (5)$$

and the relative uncertainty in the concentration is given by

$$\frac{\Delta C}{C} = \frac{\Delta T}{T' (\ln T' + \ln T_r)} \quad (6)$$

where T' is the transmittance relative to the reference solution and T_r is the transmittance of the reference solution. If the transmittance of the reference solution relative to solvent is 0.368 or smaller, the denominator $T'(\ln T' + \ln T_r)$ increases with T' and $\Delta C/C$ has a minimum value when T' equals unity. In terms of absorbance, provided the absorbance of the reference solution relative to solvent is 0.4343 or larger, the absorbance of the unknown sample relative to reference should be as small as possible.^{9, 15, 23}

It should be emphasized that the above treatment only relates the relative uncertainty in concentration error to the inherent uncertainty, ΔT , in reading the spectrophotometer scale based on the assumption that ΔT does not vary with T . The actual uncertainty, ΔT , in measuring the transmittance may be caused by many factors, not all of which are independent of T . Cahn¹⁰ in a report on photometric reproducibility showed that for the Cary, Model 11, and Beckman DU spectrophotometers, the standard deviation in absorbance, σ_A , appeared to be independent of A , at least up to an absorbance of 1.0, which would mean that over the corresponding transmittance range, ΔT was proportional to T . This would not invalidate differential spectrophotometric methods as suggested by Crawford¹¹ except insofar as these methods depended entirely on a "scale expansion" for any increase in precision which is the distinctive feature of the two-reference method described below.

A two-reference differential spectrophotometric method has been suggested by Reilley and Crawford²⁹; Gridgeman¹⁴ also mentioned the possibility of using such a method in a brief review article on differential absorptiometry. This method is based, in terms of Equation 1, on an attempt to increase the SC product by increasing S . The spectrophotometer is set at both the 100% T and 0% T ends of the scale with solutions of concentration C_1 and C_2 in the light path, respectively. The effect of this, as demonstrated in Figure 1 by curve III, is to greatly expand the instrument scale and thus reduce the error, ΔC , for a given error in absorbance, ΔA . Theoretically, the smaller the difference in transmittance of the reference solutions, the more precise the method becomes. Still another method was proposed by Reilley and Crawford²⁹ which is essentially a variation of the two-reference method for use with very dilute solutions. In this method, the instrument is balanced as usual at 100% T

with solvent but then balanced at 0% T with a dilute reference solution in the light path.

Banks, Spooner, and O'Laughlin^{3, 4} applied the two-reference method to the analysis of lanthanon mixtures and observed a significant increase in the relative precision of concentration measurements over that obtained by conventional spectrophotometric methods. The standard deviation by conventional methods was about 1% while with the two-reference method it was 0.21% with reference solutions having a transmittance span of about 0.2 and a transmittance relative to solvent near 0.38. It was observed, however, that the standard deviation was not lowered significantly when the transmittance span was made smaller, but was lowered significantly when the transmittance of the reference solutions relative to solvent was decreased. This suggests the decrease in the standard deviation observed may have been largely due to the use of a relative method, i.e., the measurement relative to a reference solution, which compensates for errors such as those due to incorrectly adjusting the spectral position and not to the scale expansion feature of the method. The data obtained by Banks, Spooner, and O'Laughlin^{3, 4} do not verify the usefulness of the two-reference method as reported. Whether the method has any advantage over the one-reference method in this case is questionable. Recently, Shigematsu and Tabushi³⁸ also reported that the two-reference method proposed for use with dilute solutions, i.e., the trace analysis method, gave no better precision than conventional methods.

The use of the two-reference method would be advantageous only if the same increase in precision of concentration measurement could be achieved using two reference solutions with transmittances close to 0.368 as could be obtained with the one-reference, or transmittance-ratio, method which requires a reference solution of much lower transmittance for the maximum gain in

precision. The two-reference method certainly increases the slope, S , as illustrated in Figure 1, but the stability of the instrument decreases as the concentration difference between the two reference solutions is decreased. Consequently, ΔA becomes larger. The criterion of whether the method will reduce the relative uncertainty in the concentration measurement is whether the ratio of ΔA to S becomes smaller. If highly absorbing reference solutions are required, there is no advantage in using the two-reference method over the transmittance-ratio method because the former is considerably more time consuming.

The two-reference method has the further disadvantage that the scale reading observed is not a simple function of the concentration. This makes it necessary to construct a nonlinear calibration plot or resort to plotting an exponential function of the concentration against the scale reading. Even in the latter case, a linear plot results only if the photocell responds in a linear manner. Slight shifts in instrumental characteristics would necessitate recalibration of the working curve, an onerous task in case of a nonlinear plot.

Ringbom and Österholm²² suggested a differential method which is based on the deflections of the galvanometer needle of a two-photocell filter photometer when a known volume of solvent, and then a known volume of the sample solution, are added to the same reference solution. This method is similar in some respects to both the two-reference method proposed by Reilley and Crawford²⁹ and an analyte addition technique^{22, 27} which was severely criticized by McBryde²⁶ and Crawford.¹¹ Although the experimental results obtained by Ringbom and Österholm²² showed good precision, this seems more likely a tribute to the experimental skill of the authors than to the merits of the method.

The compensation of systematic errors which is inherent in the use of a differential method may well be equally as important as

the theoretical increase in precision obtained with this technique. The great improvement in precision observed by Kortüm when he employed a comparison method, as already pointed out, was undoubtedly due to just such a compensation of systematic errors. The one-reference, or transmittance-ratio, differential method inherently gives a high degree of compensation of systematic errors when the absorbances of the sample and reference solution are approximately equal. The two-standard method, in general, will not give as high a degree of compensation of systematic errors unless the absorbances of the reference solutions are extremely close together or are quite high. Neither of the latter alternatives is very practical for the reasons already mentioned.

An interesting application of differential methods has been made to the indirect spectrophotometric determination of fluoride.^{23, 24} In indirect spectrophotometry, the substance to be determined, usually the fluoride ion, is added to a colored solution which is bleached. The extent of the bleaching can be related to the amount of the substance added. Ideally, the bleaching of the colored solution will be directly proportional to the amount of the bleaching agent added. Usually, however, because of the finite value of the equilibrium constants involved, the relationship is not linear but falls off when nearly stoichiometric amounts of the bleaching agent are added.

Lothe²³ reports that several previous authors had been so convinced that low absorbance errors were synonymous with high photometric error that they insisted on keeping the absorbance of the bleached samples above 0.25. This certainly is carrying the idea that absorbance readings must be near the "magic number" of 0.43 to the ridiculous extreme, if this was the reason. Lothe actually goes on to show that, in an ideal case, the optimum absorbance of the sample solution in indirect spectrophotometry is zero.

Lothe²³ developed an equation relating the

relative concentration error $\Delta C_i/C_i$ of the bleaching agent (fluoride) to the transmittances of the bleached solution T_i , and the unbleached original solution T_u , i.e.,

$$\frac{\Delta C_i}{C_i} = \frac{\Delta T_i}{T_i (\ln T_i - \ln T_u)}. \quad (7)$$

A very similar equation results when a differential method is applied and the instrument balanced at the 100 % transmittance end of the scale with a reference solution slightly more bleached than the sample solution,

$$\frac{\Delta C_i}{C_i} = \frac{\Delta T_i'}{T_i' (\ln T_i' - \ln T_u)}. \quad (8)$$

The previous equations are for the ideal case where the extent of bleaching is proportional to the amount of bleaching agent added and were deduced by arguments analogous to those used in arriving at Equations 4 and 6. For easier comparison with Equations 4 and 6, the form and symbols in in Equations 7 and 8 have been changed from that given by Lothe.

Actually, because the equilibrium constant for the bleaching reaction has a finite value, the slope of the absorbance-concentration plot levels off as the extent of bleaching approaches 100 %. Consequently, the optimum absorbance for the bleached sample solution is not zero as in the ideal case, but some higher value. Lothe^{23, 24} derived equations involving the various equilibrium constants which can be used to predict the optimum absorbance for any given values of the constants involved.

The shape of the absorbance-concentration plot in an actual application of an indirect method will approximate the inverse of curve I in Figure 1. The slope will be negative rather than positive and gradually flatten out as the absorbance becomes smaller. Equation 1 can also be used to predict the optimum conditions for minimum relative error in this case. The minimum relative error will occur when the absolute

value of the slope-concentration product is a maximum.

The use of a differential method in the above case permits the open end of the spectrophotometer scale to be used without requiring that the bleaching be almost 100 % complete. This is an advantage because the slope of the absorbance-concentration curve usually becomes very small when the colored solution is nearly completely bleached. It can be seen from inspection of Equations 7 and 8 that the denominator of the right hand side of both equations increases as T_i or T_i' increases and as T_u decreases. If ΔT_i or $\Delta T_i'$ is assumed to be constant, the larger the magnitude of the denominator, the smaller the relative uncertainty in the determination of the concentration of the bleaching agent. The largest value T_i or T_i' can have is unity, i.e., an absorbance of zero, but the transmittance of the original unbleached solution can be made as small as the color system involved permits. There is no instrumental limit on how high the absorbance of the unbleached solution is made because, in indirect spectrophotometry, it is not necessary to make any spectrophotometric measurements on the unbleached solution. This is an important advantage of an indirect method over the direct transmittance-ratio method because in the latter method, it is necessary to balance the spectrophotometer on a highly absorbing reference solution. Consequently, it would appear that there is no instrumental limit to the possible gain in relative precision in concentration measurements by an indirect method. The differential technique should certainly be employed because its use will result in the compensation of systematic errors and also permit the open end of the spectrophotometer scale to be used without any sacrifice in sensitivity.

Recently, Reilley and Hildebrand³⁰ advanced what they considered two new methods of indirect differential spectrophotometry. In one of these methods, the

instrument is balanced on 100 % T with the unknown bleached sample and the relative absorbance of the unbleached standard read. In the second method, the instrument is balanced at 100 % with the unknown bleached sample and the relative absorbance of a standard bleached sample (less bleached than the unknown) then read. The concentration of the unknown is then calculated from the relative absorbance observed for the unbleached or partially bleached solutions. The only advantage claimed for these methods is that the resulting absorbance-concentration plots will be analogous to the plots obtained by the conventional and transmittance-ratio methods. The obvious disadvantages of the methods would certainly seem to far outweigh the advantages. It might also be noted that these authors incorrectly ascribed the increase in precision possible in the indirect differential method described by Lothe²⁸ to an expansion of the spectrophotometric scale.

Development of a Differential Method. The usual objective, when differential spectrophotometry is considered, is the development of a rapid, accurate analytical method. The particular method decided upon is largely determined by whether speed or accuracy is more important, the particular nature of the sample, and the instrumentation available. The development of a differential method will be considered in a rather general manner emphasizing possible sources of error. Only the transmittance-ratio method will be considered.

The choice of the color system, as in any spectrophotometric method, is largely determined by the nature of the sample and the possible interferences. If there is any choice in the matter, it is well to avoid using an absorption band at either high or low wavelengths because stray radiant energy becomes a greater problem at these wavelengths. The higher the molar absorptivity, ϵ , the greater the slope, S , of the absorbance-concentration plot; but the slope-concen-

tration product, SC , is the quantity which should be made a maximum and not either S or C singly. The manner in which the slope varies with concentration, the amount of sample available, and the equipment available are other important considerations in selecting a color system.

The optimum concentration of the reference solution may be determined experimentally in the following manner. A group of standard solutions is prepared with increasing concentration in which the concentration increment, $C_i - C_{i-1}$, between any two adjacent solutions is the same. The spectrophotometer is balanced on the more dilute of one of the above solutions, C_{i-1} , and the relative absorbance, A_i , of the next more concentrated solution is determined. This is repeated until all the solutions in the group are read or until it is no longer possible to balance the spectrophotometer because the solution to be used as reference is too highly absorbing.

The spectrophotometer should be balanced by adjusting the slit width. The optimum sensitivity setting should be selected initially and then not changed. The reason for not changing the sensitivity control is that this may change ΔA which is assumed to be constant. Practically, it is easier to make the final fine adjustment in balancing the spectrophotometer with the sensitivity control and this is usually done. The change in ΔA by small adjustments with the sensitivity control on an instrument such as the Beckman DU is probably not significant. However, large changes in the sensitivity control, or changes in the dynode voltages if a photomultiplier attachment is used, may affect ΔA and make it difficult to interpret the results obtained in the manner described above.

If the relative absorbances, i.e., the A_i values, obtained are divided by the concentration increment, $C_i - C_{i-1}$, an average value for the slope, S , of the absorbance-concentration plot is obtained for the con-

centration range bounded by the two solutions. The slope is usually constant for the more dilute solutions but begins to fall off as the concentration of the reference solution increases. This will usually occur whether Beer's law is followed or not because as the slit width is increased, the band width of radiant energy passed by the slit increases and Beer's law strictly applies only for monochromatic radiation.

The optimum concentration for the reference solution is that concentration for which the slope-concentration product, SC , is a maximum. This always occurs after the slope begins to decrease. Consequently, it is important to note that the plot of absorbance versus concentration of more concentrated solutions read relative to this reference will not be linear, though over a small concentration range it may be approximately linear. The latter statement is true because, even at the same slit width, the apparent molar absorptivity will decrease with an increase in absorbance of the sample read unless the radiant energy is perfectly monochromatic, a condition obviously far from prevailing when a wide slit is employed. Consequently, a calibration plot should be constructed in which standard solutions are read relative to the reference chosen. The optimum condition is, of course, that the unknown have exactly the same absorbance as the reference, but in practice, a concentration range must be established within which the unknown will fall. If the difference in the absorbances of the unknown and the reference is no greater than 0.2 to 0.3 absorbance unit, no significant decrease in precision results, provided a calibration plot is constructed. This usually gives a large enough concentration range to make the method practical.

Because the absorbance-concentration plot for solutions read relative to a reference solution of "optimum" absorbance is not linear, it is often convenient to use a somewhat less highly absorbing reference solution.

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This will result in a more linear calibration plot, especially desirable if a rather wide concentration range is desired. A reference solution with a lower than "optimum" absorbance may also be necessary because of sample limitations, color stability or similar reasons.

The various factors which may affect the results in ordinary spectrophotometry such as those listed by Mellon²⁸ or Gibson¹³ should be kept in mind when a differential method is employed. It would be unnecessarily repetitious to discuss how all of the factors considered by the above authors might affect differential spectrophotometric methods, but it seems advisable to list these factors and discuss several which are most likely to lead to serious errors, when using differential methods.

Mellon²⁸ lists: solvent effect; pH; concentration effects; temperature; interfering ions, both because of color and ionic strength effects; irradiation; redox potential; effect of dissolution aids; component interaction; hydrolysis; light fading; fluorescence; turbidity; and plating of the colored dye on the cuvet faces as factors which may affect the absorption spectrum. When a differential method is used, many of these factors tend to affect the sample and reference to the same extent and there is a compensation of errors. If the reference and sample are not treated exactly alike, certain factors are more troublesome than others. Slight temperature differences between the reference solution and sample solution can lead to significant errors. The fact that the reference solution is apt to be left in the cell compartment while a series of samples are read can very easily result in an appreciable temperature difference between reference and sample solution unless adequate precautions are taken.

Bastian⁸ has studied temperature effects on differential spectrophotometric methods and has shown how both the absolute value of the temperature of the sample and tem-

perature differences between sample and reference solution can lead to significant errors. The former can introduce significant errors when only the zero reference solution is used to establish the spectrophotometric scale from day to day. The absolute value of the temperature can affect the slope of the absorbance-concentration plot which will result in relative concentration errors directly proportional to the difference in absorbance of the sample and reference. This emphasizes the advisability of keeping the absorbance difference between reference and sample solution small or of running several standards at the same time as the sample. Bastian has also shown that the temperature differential between reference and sample solution in the specific case of the copper perchlorate system, must be less than 0.13°C if the relative concentration error is to be 0.5 part per thousand or better. The latter type error, i.e., a temperature difference between the sample and reference solution, is usually more serious and great care should be exercised in differential spectrophotometry to insure that the temperature of the reference and sample solutions are the same when measuring the relative absorbance.

The relative position of the cuvetts containing sample and reference in the light beam is important if the color system employed exhibits fluorescence. If the distance of the two cuvetts from the phototube is unequal, a significant error can be introduced. Gibson¹³ has reported that the magnitude of any error caused by fluorescence is also dependent on the design of the spectrophotometer employed.

Slow hydrolysis of the substance studied may also lead to significant errors in relative concentration measurement. Particular attention should be given to this possibility when the reference solution is prepared in quantity and allowed to stand for long periods of time.

Obviously, any of the other factors listed above can also cause significant errors unless

both sample and reference solution are in the same physical and chemical state. The necessity for careful control of temperature illustrates how easily inaccurate results can be obtained.

Cuvet Corrections. Slight differences in the lengths and absorptivities of the cuvetts used are not too important in ordinary spectrophotometry because the better cuvetts are usually accurate to within several parts per thousand and precision of better than 0.5 to 1% is not required. Differences in the lengths of the cuvetts can easily be the limiting error in the case of a differential method, however, unless an accurate correction can be made.

In the case where two cuvetts are used, it is not sufficient to merely measure the absorbance difference observed when both cuvetts are filled with the reference solution and one is read relative to the other as is customary in ordinary spectrophotometry. This will take care of any differences in the absorptivity of cuvetts themselves, but will not correct for errors caused by any differences in the lengths of the cuvetts containing the reference solution and the sample.

The correction for differences in cuvet lengths is a linear function of the absorbance and the necessary correction can be obtained in the following manner. Both cuvetts are filled with the reference solution and, after balancing the instrument with one cuvet in the light path, any absorbance difference is observed. This is repeated with the most concentrated solution to be determined in both cuvetts. The absorbance difference in this case will be different if the cuvetts are not perfectly matched for length. The absorbance differences observed are then plotted as a function of the corresponding absorbances of the solutions in the cuvetts. If the correction is small, these two measurements should be sufficient to establish the cuvet-correction plot but, if the correction is fairly large, it is well to repeat the above with several solutions of the intermediate concentrations. The appropriate correction, estimated from the

cuvet-correction plot and the uncorrected absorbance of the sample, is then made on the observed absorbance. Naturally, the cuvetts should be kept scrupulously clean and handled with extreme care. For the greatest possible accuracy, it would probably be desirable to devise some system where the cuvetts could be emptied and filled without removing them from the cuvet compartment.

Summary. The various methods which have been proposed for decreasing the relative error in spectrophotometric concentration measurements have been discussed in terms of the general relationship given in Equation 1. The conditions for the lowest possible relative error in concentration are as follows: for ΔA , the error in the absorbance measurement, to be as small as possible and the absolute value of the product of the concentration, C , and the slope, S , of the absorbance-concentration plot to be as large as possible. The direct methods discussed are somewhat arbitrarily divided into three groups: those which make ΔA as small as possible; those which make the SC product as large as possible primarily by varying C ; and those which make the SC product as large as possible primarily by increasing S .

The danger in assuming that an increase in spectrophotometric sensitivity, i.e., making ΔA small, will result in a decrease in the relative concentration error is forcefully illustrated by Kortüm's work.²⁰ Although Kortüm was able to measure the absorbance very precisely, this alone did not mean he was able to determine the concentration with equal precision. The apparent reason was that the relation between the measured absorbance and concentration varied with time and it was only when he determined this relation at the same time and under exactly the same conditions as he used to measure the absorbance of the sample that any significant decrease in relative concentration error was observed.

The two-reference method proposed by Reilley and Crawford²¹ is discussed in terms

of Equation 1 as a method which makes the slope, S , as large as possible. The assumptions on which this method is based are that the principal source of error is the scale reading error and that any technique which makes the relative concentration error less sensitive to a given scale reading error will lead to a decrease in the relative concentration error. The validity of the first assumption is questionable.^{10, 20} Furthermore, the manner in which the slope is increased, by balancing the spectrophotometer on two reference solutions at both ends of the scale, causes the instrument to become more unstable as the transmittance difference between the reference solutions is decreased and ΔA increases, thus defeating the primary objective.

The transmittance-ratio method, which makes the product, SC , large primarily by increasing C , has been experimentally shown to lead to a significant decrease in relative concentration error.^{1, 2, 5, 6, 7, 8, 9, 12, 25, 28} This method requires no special instrumentation and the spectrophotometer is not used in such a way that it becomes unstable as in the case of the two-reference method. The practically simultaneous comparison of reference and sample solutions of approximately the same concentration results in the compensation of systematic errors. This compensation of errors may well be a more important factor in differential spectrophotometric measurements than any theoretical gain in precision.

The "ultimate method" for improving the precision of concentration measurements based on spectrophotometric data may be an indirect method because with this technique there are no instrumental limitations on the concentration of the substance being determined. Unlike the direct transmittance-ratio differential method, there is no necessity for balancing the spectrophotometer on a highly absorbing reference solution. The absorbance of the bleached solution which is actually read in an indirect method should

be rather low and, in the ideal case, would be zero. Actually, it is much better to balance the spectrophotometer at zero absorbance with a reference solution slightly more bleached than the sample solution. This is particularly advantageous when the equilibrium constants involved are such that the absolute value of the slope of the absorbance-concentration plot decreases rather rapidly as the extent of bleaching approaches 100%. The use of a differential method, i.e., balancing the spectrophotometer with a slightly more bleached reference solution, permits the open end of the spectrophotometer scale to be used without the requirement that the colored solution be almost completely bleached. It also results in the compensation of systematic errors which, in this case, is probably the more important reason for using a differential method.

Practically, the application of an indirect differential method to the precise spectrophotometric determination of major constituents in a sample may be severely limited by the lack of suitable color systems. The chief applications of the indirect method have been made in the determination of the fluoride ion. Lothe²⁴ reported very good precision for the determination of fluoride by an indirect differential method with the percentage standard deviation only 0.2% when the fluoride concentration was 500 γ per 50 ml. The chief source of error in the method used by Lothe was very probably chemical, a large pH dependence, and a further increase in the fluoride ion concentration would probably not improve the precision. Provided suitable color systems were available, however, the relative precision which could be attained by indirect differential methods should be as great or greater than that attained previously with direct differential methods.

The distinction between absolute and relative spectrophotometric measurements is of paramount importance and is especially important when the purpose of the measure-

ments is the precise determination of concentration. The failure to appreciate that the relative precision in concentration measurements can be greatly increased by extremely simple means can be quite costly in time and materials. Attempts to increase the relative precision in concentration measurements by building more sensitive spectrophotometers or by using the spectrophotometer in some unorthodox manner are not only costly and time consuming, but will probably not result in any significant gain in precision. The relative precision of concentration measurements can be increased greatly by using the spectrophotometer as a null point device in comparing the sample with some known reference solution. This is the basis of methods such as the transmittance-ratio method, indirect differential methods, and spectrophotometric titrations. Even though high precision is not required, the use of a differential method often results in a compensation of systematic errors and is thus useful even in trace analysis.

REFERENCES

1. BACON, A., AND MILNER, G. W. C., *Anal. Chim. Acta*, **15**, 573 (1956).
2. BANKS, C. V., BURKE, K. E., O'LAUGHLIN, J. W., AND THOMPSON, J. A., *Anal. Chem.*, **29**, 995 (1957).
3. BANKS, C. V., SPOONER, J. L., AND O'LAUGHLIN, J. W., *Anal. Chem.*, **28**, 1894 (1956).
4. *Ibid.*, **30**, 458 (1958).
5. BARNEY, J. E., BERGMANN, J. G., AND TUSKAN, W. G., *Anal. Chem.*, **31**, 1394 (1959).
6. BASTIAN, R., *Anal. Chem.*, **21**, 972 (1949).
7. *Ibid.*, **23**, 580 (1951).
8. *Ibid.*, **25**, 259 (1953).
9. BASTIAN, R., WEBERLING, R., AND PALILLA, F., *Anal. Chem.*, **22**, 160 (1950).
10. CAHN, L., *J. Opt. Soc. Am.*, **45**, 953 (1955).
11. CRAWFORD, C. M., *Anal. Chem.*, **31**, 343 (1959).
12. GEE, A., AND DIETZ, Y. R., *Anal. Chem.*, **25**, 1320 (1953).
13. GIBSON, K. S., *National Bureau of Standards Circular 484*, "Spectrophotometry," Government Printing Office, Washington, D. C., 1949.
14. GRIDGEMAN, N. T., *Photoelec. Spectrometry Group Bull.*, **8**, 197 (1955).
15. HISKEY, C. F., *Anal. Chem.*, **21**, 1440 (1949).
16. HISKEY, C. F., AND FIRESTONE, D., *Anal. Chem.*, **24**, 342 (1952).
17. HISKEY, C. F., RABINOWITZ, J., AND YOUNG, I. G., *Anal. Chem.*, **22**, 1464 (1950).
18. HISKEY, C. F., AND YOUNG, I. G., *Anal. Chem.*, **23**, 1196 (1951).
19. HUGHES, H. K., *Anal. Chem.*, **24**, 1349 (1952).
20. KORTUM, G., *Angew. Chem.*, **50**, 193 (1937).
21. KORTUM, G., AND SEILER, M., *Angew. Chem.*, **52**, 637 (1939).
22. LEROY, G., *Ann. fals. et fraudes*, **10**, 208 (1917).
23. LÖTHE, J. J., *Anal. Chem.*, **27**, 1546 (1955).
24. *Ibid.*, **28**, 949 (1956).
25. MANNING, D. L., AND WHITE, J. C., *Anal. Chem.*, **27**, 1389 (1955).
26. MCBRYDE, W. A. E., *Anal. Chem.*, **24**, 1639 (1952).
27. MELLON, M. G., "Analytical Absorption Spectroscopy," p. 110, Wiley, New York, 1950.
28. *Ibid.*, p. 314.
29. REILLEY, C. N., AND CRAWFORD, C. M., *Anal. Chem.*, **27**, 716 (1955).
30. REILLEY, C. N., AND HILDEBRAND, G. P., *Anal. Chem.*, **31**, 1763 (1959).
31. RINGBOM, A., *Z. anal. Chem.*, **115**, 332 (1939).
32. RINGBOM, A., AND ÖSTERHOLM, K., *Anal. Chem.*, **25**, 1798 (1953).
33. SHIGEMATZU, T., AND TABUSHI, M., *Bull. Institute for Chemical Research, Kyoto University*, **36**, 127 (1958).
34. STEELE, T. W., *Analyst*, **83**, 414 (1958).
35. WHITE, J. C., MEYER, A. S., AND MANNING, D. L., *Anal. Chem.*, **28**, 956 (1956).

JEROME W. O'LAUGHLIN AND
CHARLES V. BANKS

FATS, OILS, FATTY ACIDS, AND GLYCERIDES
(Ultraviolet Spectroscopy)

Emphasis on the application of chemical spectroscopy today is centered on the use of newer tools, on extensions of the electromagnetic spectrum, or on techniques employing these radiations in differing ways. Thus we attend a symposium on the application of ultraviolet atomic absorption, or read papers describing applications of molecular fluorescence. We learn about nuclear magnetic resonance spectroscopy and the advantages of combinations of gas-phase chro-

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matography with mass or with infrared spectroscopy. In this continual expansion of spectroscopy to provide new tools for the analytical chemist, the use of ultraviolet molecular absorption is almost overlooked. The fact remains, however, that with emission analysis, ultraviolet molecular absorption is the oldest branch of spectroscopy to be applied to the problems of the analytical chemist and is, perhaps, still making a greater over-all contribution than any other branch of spectroscopy.

The ultraviolet region is defined as that portion of the electromagnetic spectrum just above about 20 Å to about 400 millimicrons. Below 20 Å radiation arises from transitions of inner-orbital electrons, that is x-ray spectra; above 400 millimicrons the human eye becomes a detector and the portion of the electromagnetic spectrum above this wavelength is visible spectra. However, in practical applications of ultraviolet, measurements must be confined mainly to the limits 220 to 400 millimicrons as below

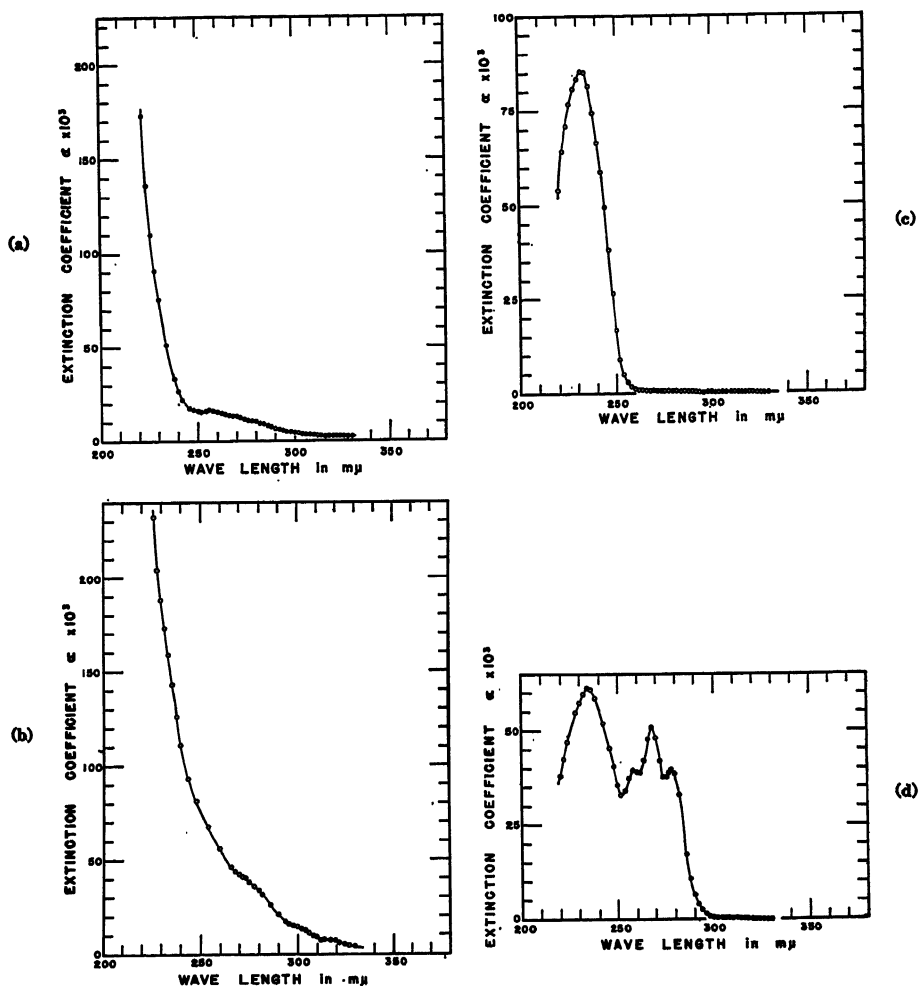


Fig. 1. Ultraviolet absorption spectra: (a) and (c) noncharacteristic absorption of linoleic and linolenic acids, respectively; (b) and (d) characteristic absorption of alkali-isomerized linoleic and linolenic acids, respectively.

220 millimicrons several factors contribute to decrease its usefulness. Among these are the fact that at about 220 millimicrons: (a) air begins to absorb; (b) quartz, the usual material for optics in the ultraviolet region, exhibits absorption; (c) the photoelectric detectors become less sensitive; and (d) the light sources, i.e., the hydrogen discharge lamp, become weaker. Considerable interest has been shown in extending this region, 220 to 400 millimicrons, to include the range of ethylenic absorption from 170 to 220 millimicrons for analytical applications. With instruments equipped with special types of detectors sensitive to short wavelength ultraviolet radiation and with suitably intense light sources, a wavelength of 170 millimicrons can be reached by purging the instrument with a gas more transparent to these wavelengths than air, for example, pure nitrogen. This has been done in a few applications of ultraviolet absorption spectroscopy to fatty acid materials and in this article the ultraviolet will be defined as the region of the electromagnetic spectrum extending from about 170 to about 400 millimicrons.

Examination of the ultraviolet absorption spectrum of various molecules shows that they can be divided into two classes: (a) compounds exhibiting smooth absorption usually increasing toward shorter wavelengths, called noncharacteristic or nonselective absorption and (b) those molecules exhibiting spectra consisting of one or more regions of maximum absorption called characteristic or selective absorption. In Figure 1, a and b, the ultraviolet spectra of linoleic and linolenic acids represent examples of noncharacteristic absorption. Examples of characteristic absorption are illustrated by the spectra of *alpha*- and *beta*-eleostearic acids in Figure 2. The steeply increasing noncharacteristic absorption toward shorter wavelengths, in Figure 1, a and b, arises as end-absorption from intense absorption maxima of the C=C and of the COOH

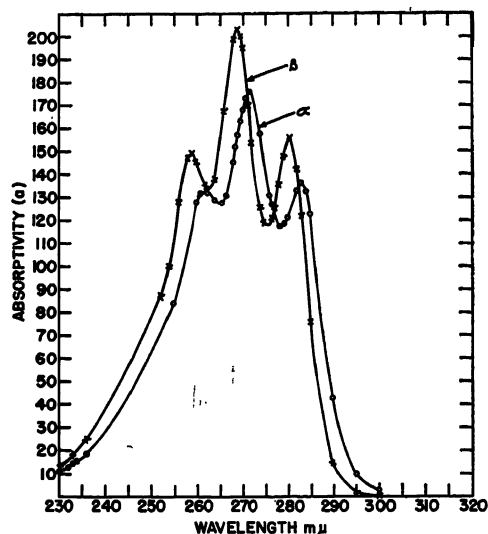


FIG. 2. Ultraviolet absorption spectra of cyclohexane solutions of *α*- and *β*-eleostearic acids.

groups below 200 millimicrons. While the magnitude of noncharacteristic absorption might indicate the presence and amount of these components, this type of absorption is generally of no value for analytical purposes and will not be considered here.

Further examination of the ultraviolet spectra of various molecules reveals that with only a few exceptions (which will be referred to later) characteristic absorption is observed only if the compound is unsaturated and contains conjugated double bonds, i.e., $-\text{C}=\text{C}-\text{C}=\text{C}-$, $-\text{C}=\text{C}-\text{C}=\text{O}$, etc. Conjugation of two unsaturated linkages forming the conjugated dienoic system, $-\text{C}=\text{C}-\text{C}=\text{C}-$, gives rise to an absorption band of considerable intensity in the region of 230 millimicrons. The exact position of this maximum can be calculated by means of Woodward's rule. This rule, which applies to acyclic conjugated dienes, assigns a value of 5 millimicrons to be added to the position of maximum absorption for the simplest conjugated diene (butadiene, ca. 217 millimicrons in isooctane solution) for each alkyl substituent linked to the diene chromophore. Extension of the conjugated

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system to a trienoic conjugation, —C=C—C=C—C=C— , results in a shift in the absorption to about 268 millimicrons, while a tetraenoic system absorbs with maximum at about 315 millimicrons, pentaenoic at about 346 millimicrons, hexenoic at about 374 millimicrons, etc. Continuation of the conjugated system shifts the absorption into the visible region of the electromagnetic spectrum and accounts for the characteristic color of many natural commodities. Hewitt's rule, which has been known since 1907, states that the longer the conjugated system, the deeper (i.e., more toward the red) the color.

From these observations it might be concluded that ultraviolet absorption spectroscopy is limited to investigations of those molecules which contain polyunsaturation at least a portion of which is conjugated. Thus all aromatic compounds, but only a relatively small per cent of the long-chain aliphatic compounds encountered in fatty acid chemistry, would be amenable to this technique. That is a serious limitation to the study of long-chain fatty acids, esters, and their glycerides and other derivatives by ultraviolet absorption. Saturated and mono-unsaturated compounds usually cannot be investigated by means of ultraviolet spectroscopy. However, nonconjugated polyunsaturated molecules are not always excluded, for simple analytical pretreatment does, in favorable cases, permit a rearrangement of the double bonds into conjugation and measurement by means of ultraviolet spectroscopy.

While conjugations of various combinations of unsaturated linkages have limited usefulness, the specific conjugation of two or more ethylenic linkages occurring naturally (performed conjugation) or after suitable analytical pretreatment of the sample (isomerized conjugation) account for the great majority of successful applications of ultraviolet absorption spectroscopy in fat and oil chemistry. An ultraviolet spectrum of an

unknown fat or oil can yield considerable information regarding its composition. It can be used to determine: (a) whether the particular sample contains any unsaturated conjugated material; (b) if conjugated substances are present, the order of conjugation, i.e., diene, triene, etc.; (c) if there is evidence of diene conjugations, application of Woodward's rule will furnish some evidence as to the nature of the substituents; (d) particular characteristics of the ring triene conjugation of aromatic molecules can be recognized and the presence or absence of this class of compounds established; and (e) conjugation in nonaromatic rings gives rise to characteristic absorption bands which can be recognized and analyzed by extensions of Woodward's rule to nonaromatic cyclic compounds. Hence ultraviolet absorption spectroscopy has been serving the lipide chemist faithfully for some time and even with extensions of analytical spectroscopy to other regions of the electromagnetic spectrum and the development of new uses of these radiations in various ways to give rise to entirely new tools of spectroscopy, ultraviolet absorption is likely to remain a most important technique for the fatty acid chemist.

Quantitative Applications to Problems in Fat and Oil Chemistry

Single-Component Analysis: Determination of Vitamin A. Most applications of ultraviolet absorption spectroscopy to fatty acid chemistry have been quantitative in nature as this tool lends itself readily to accurate and sensitive quantitative measurements. Quantitative analysis by ultraviolet spectrophotometry is based on the laws of Bouguer and of Beer. These two laws can be conveniently combined into the single expression:

$$a = A/bc \quad (1)$$

whence:

$$c = A/ab \quad (2)$$

where a is a constant characteristic of the

absorbing medium, called the absorptivity. For a pure compound, a , when measured with an instrument which permits sufficient resolution, is a constant characteristic of the specific compound. If the absorbance A of the pure compound is measured with an ultraviolet spectrophotometer in a cell b cm long in solution in a suitably transparent solvent at a concentration of c grams per liter, a can be calculated from equation (1). Once established, the value of a can be used for measurements made on solutions containing unknown quantities of the same absorbing component, by means of equation (2), provided only that these measurements are made under the same conditions, i.e., identical optical and electronic settings of the instrument.

The single component method of analysis can be illustrated by the determination of vitamin A. This compound exhibits a spectrum with a characteristic maximum at 325 millimicrons (Figure 3). Once the absorptivity of the pure vitamin A is determined, measurements of samples containing it can be made very rapidly. Details of the specific procedure are given in the Association of Vitamin Chemists' Method of Vitamin Assay.¹ Luckmann and his co-workers² reported extensive investigations of this analysis for the determination of vitamin A in fortified fats, particularly margarine, and concluded that "... the spectrophotometric method is the most reliable procedure for assaying margarine for vitamin A following fortification with quality vitamin A concentrates. It is far more precise than the biological assay and equally as specific for vitamin A ...". If the unfortified material is available, the determination can best be made by measuring both the fortified and the nonfortified samples at 325 millimicrons and calculating the vitamin A concentration from the relation:

III U.S.P. units of vitamin A per gram

$$= (a' - a) \times 5,700 \times 1/0.3,$$

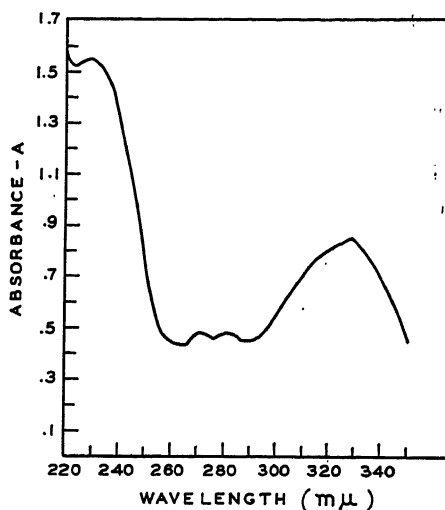


FIG. 3. Ultraviolet absorption of vitamin A.

where a' and a are absorptivities at 325 millimicrons for the fortified and nonfortified samples, respectively, 5,700 is a factor for conversion from spectrophotometric to gravimetric units and 0.3 is a factor to convert grams to U.S.P. units.

Murray and co-workers have applied the technique to show that vitamin A was reasonably stable in sesame oil.³

If the nonfortified sample is not available a correction for absorption at 325 millimicrons, not due to vitamin A, can be made by the Morton-Stubbs procedure.⁴

In this procedure extraneous absorption is corrected mathematically on the assumption that, when plotted, such absorption is a straight line across the portion of the curve being measured. Braekkan and Lambertsen⁵ used a direct measurement of ultraviolet absorption with the Morton and Stubbs correction to determine vitamin A in cod-liver and other vitamin oils. It has been adopted by the U. S. Pharmacopeia⁶ and by the Association of Official Agricultural Chemists.⁷ Details will be found also in the Association of Vitamin Chemists' Methods of Vitamin Assay.¹

To avoid mathematical corrections, when a nonfortified sample is not available, some

workers suggested a prior chromatographic treatment to remove interfering absorption. Wilkie⁸ used magnesia to purify margarine extracts, but subsequent tests of his method revealed that the resulting extract does not exhibit a spectrum typical of vitamin A.⁹ Boldingh and Drost¹⁰ used a twin chromatographic column, the first portion alumina, the second alkali-treated alumina, and obtained a purified extract with a spectrum identical to that of pure vitamin A. Braekkan and Lambertsen¹¹ simplified this procedure by combining the two adsorbents into a single column and obtained comparable results. Rosner and Kan⁹ maintained that the alkali alumina alone was sufficient and Lord and Bradley¹² argued against the use of any activated adsorbent as nonreproducible, and urged the use of natural bone meal. However, their choice of a natural product has likewise been criticized as nonreproducible.^{12b} Wilkie and Jones¹³ reviewed the importance of a reproducible adsorbent and published procedures for the standardization of alumina and magnesia mixtures used in vitamin A chromatography. Friedman¹⁴ has reported the results of collaborative testing by the Association of Official Agricultural Chemists on the determination of vitamin A in oleomargarine fortified with carotene and vitamin A, and briefly reviewed the collaborative testing by this Society over a period of fifteen years. As a result of latest collaborative tests, a procedure using the standardized alumina adsorbent, with an additional requirement of magnesia-“Celite” chromatography if the final extract is colored, has been recommended for adoption by the AOAC. Details of the procedure are given in Friedman’s report.

The problem of obtaining agreement in vitamin A assay by direct ultraviolet spectrophotometry with bioassays is complicated, as pointed out by Morton and Bro-Rasmussen,¹⁵ by the occurrence in natural products, particularly fish oils, of three vitamin A active substances, all *trans* vi-

tamin A, neovitamin A₁, and vitamin A₂. Bro-Rasmussen, Hjarde and Porotnikoff¹⁶ have proposed a method involving a separation of all three components on dicalcium phosphate columns and their separate determination by ultraviolet spectrophotometry, illustrating the method with the analysis of fish oils. Tsuchiya and Kaneko,¹⁷ and Kamath and Magar¹⁸ have shown that Japanese and Indian fish oils exhibit spectra similar to that of vitamin A fortified cottonseed oil.

Vitamin D, like vitamin A, exhibits an ultraviolet spectrum with a characteristic absorption band. This characteristic band with a maximum of 265 millimicrons can be used to detect and determine vitamin D content of natural or irradiated fats and oils. Brockmann and his co-workers¹⁹ have shown that vitamin D₂ (irradiated ergosterol) and vitamin D₃ (activated 7-dehydrocholesterol) have the same absorption curves and identical absorptivities. Direct determination of vitamin D₂ content by measurement of the intensity of the band at 265 millimicrons has been reported by Reerink, van Wijk and van Niekerk,²⁰ Töpelmann and Schuhknecht,²¹ and Ol’Khin.²² Marcussen²³ used hydraffin K₄ and Ewing and co-workers²⁴ “Superfiltrol” as adsorbents in a chromatographic purification in the analysis of vitamin D in irradiated corn oil and fish liver oils which contained interfering vitamin A and provitamin A (carotene). Ewing and co-workers^{24b} also reported a satisfactory determination of vitamin D₂ in the presence of vitamin A, using a two-step chromatographic process, the first step employing “Superfiltrol,” the second activated alumina.

Single-Component Analysis: Determination of Alpha-Eleostearic Acid. Another example of a single-component analysis in the field of fatty acid chemistry is the determination of eleostearic acid (9,11,13-octadecatrienoic acid) in tung oil. Tung oil owes its particular properties as a drying oil to the presence of about 80 % of alpha-eleostearic acid. In fresh, or so-called

alpha-tung oil, this acid occurs as the alpha-isomer only. The structure of alpha-eleostearic acid has been established mainly from infrared absorption measurements reported independently by two groups (^{25, 26}) as 9-*cis*, 11-*trans*, 13-*trans*-octadecatrienoic acid. It is thus a naturally occurring triene conjugated compound.

Estimations of the quality of tung oil have been made by a long, tedious, and not entirely satisfactory determination of eleostearic acid by empirical calculations from maleic anhydride addition reactions. Application of the single-component method for the determination of this constituent in alpha-tung oil is extremely rapid. As shown in Figure 2, the spectrum of this compound exhibits three characteristic maxima, the most intense occurring at 271.5 millimicrons (in cyclohexane solution). A few milligrams of the oil are accurately weighed into a small volumetric flask, dissolved in and brought to volume with cyclohexane and a single spectrophotometric measurement made at 271.5 millimicrons. Calculation of the concentration of alpha-eleostearic acid in the prepared solution can be made by the simple relation, derived from equation (2) above, where 168.6 is the absorptivity which has been established for pure alpha-eleostearic acid in cyclohexane:²⁷

$$c = A/168.6 \times b \quad (3)$$

The complete analysis can be made in a few minutes as compared to the day-long maleic anhydride addition method. No other component of fresh tung oil contributes to the absorption at 271.5 millimicrons and no corrections for interferences are required. Thus we have an excellent illustration of a direct, simple, single-component ultraviolet absorption analysis for the fatty acid chemist.

Multicomponent Analysis: Determination of Alpha- and Beta-Eleostearic Acid in Tung Oil. As tung oil ages, its viscosity may increase and it may under certain conditions become solid. This change

is promoted by trace quantities of certain catalysts such as iodine, selenium, sulfur, etc. The change is due to an isomerization of alpha-eleostearic acid to the beta-isomer and the resulting oil is known as beta-tung oil. The configuration of the beta-isomer has been established^{25, 26} as 9-*trans*, 11-*trans*, 13-*trans*-octadecatrienoic acid. The ultraviolet absorption of beta-eleostearic acid is similar, but not identical, to that of alpha-eleostearic acid (Figure 2), and there is a considerable difference in the absorptivity values at the positions of maxima for both isomers. In beta-tung oil both isomers are present. As the absorption of each contributes to the other, neither can be determined independently. However, both can be quantitatively measured simultaneously by the technique known as spectrophotometric multi-component analysis. All that is required is a knowledge of the absorptivity of the alpha-isomer (preferably at a position of one of its maximum absorption bands) and the absorptivity of the beta-eleostearic acid at this position; and, similarly, the absorptivity of the beta-isomer at one of its maxima where the absorptivity of the alpha-eleostearic acid is known. The required absorptivities have been re-evaluated recently²⁸ for cyclohexane and for 99 % ethanol solutions. For cyclohexane they are:

At 271.5 millimicrons
alpha-eleostearic acid (max.): $a = 176.7$
beta-eleostearic acid : $a = 168.0$

At 269.0 millimicrons
beta-eleostearic acid (max.): $a = 201.8$
alpha-eleostearic acid : $a = 157.3$

Therefore:

At 271.5 millimicrons the total measured absorptivity of the sample will be:

$$176.7 \times \% \text{ alpha-acid} + 168.0 \times \% \text{ beta-acid} \quad (4)$$

and:

At 269.0 millimicrons the total measured absorptivity of the sample will be:

$$201.8 \times \% \text{ beta-acid} + 157.3 \times \% \text{ alpha-acid} \quad (5)$$

Simultaneous solution of equations (4) and (5) and spectrophotometric measurements and calculations of the two absorptivities of the sample at the two wavelengths, permits a calculation of both alpha- and beta-eleostearic acid in the particular sample.

Thus ultraviolet spectrophotometry provides not only a much more rapid determination of eleostearic acid content in tung oil than is possible by chemical methods, but it affords a simple means for determination of the relative amounts of the two isomers, an analysis which cannot be made by chemical means, and one of considerable importance in cases where solidification of the supply of oil is of some concern.

Multicomponent Analysis: Determination of the Constituents of Sesame Oil. A second example of the use of multicomponent analysis in fatty acid chemistry is the determination of the constituents of sesame oil by Budowski, O'Connor, and Field.²⁹ The ultraviolet spectrum of sesame oil differs from that of most vegetable oils due to the presence of the components sesamin, sesamol, and sesamol in this oil. Sesamol, which occurs both in the free and in the bound form (sesamol) in sesame oil, possesses marked antioxidant activity in lard and various vegetable oils. Sesamin has been investigated for its synergistic activity with pyrethrin insecticides. Using ultraviolet absorption spectroscopy in connection with the well-known Villavecchia color reaction, Budowski *et al.* described a procedure for the simultaneous determination of the three constituents by multicomponent methods of ultraviolet spectroscopy. Suarez C and co-workers³⁰ later modified this procedure and extended it to include the analysis of sesamin concentrates. Beroza³¹ incorporated a chromatographic purification step using a silicic acid column, which is recommended particularly for samples which require large corrections for interfering absorption, such as oxidized sesame oils or oils which have been subjected to accidental alkali isomerization.

Multicomponent Analysis: Determination of Nonconjugated Polyunsaturated Fatty Acids. By all odds, the most important application of ultraviolet absorption spectroscopy to fat and oil chemistry has been the quantitative determination of nonconjugated polyunsaturated acid in fats, oil, triglycerides, and their esters, and other derivatives. These methods are all based on the principles of multicomponent analysis. The polyunsaturated acids in most fats and oils are nonconjugated and, exhibiting spectra similar to those shown for linoleic and linolenic acids in Figure 1, a and b, are not amenable to spectrophotometric analysis.

In 1943 Mitchell, Kraybill, and Zscheile³² described an isomerization procedure for the direct determination of linoleic and linolenic acid content of vegetable and animal fats and oils by means of multicomponent analysis based on the observations of Dann and Moore³³ that linoleic and linolenic acids are respectively isomerized to conjugated dienoid and to mixtures of conjugated dienoid and trienoid acids by heating with alcoholic potassium hydroxide, and of Kass, Miller, and Burr³⁴ that this isomerization is effected much more rapidly at higher temperatures, i.e., with the use of a solution of alcoholic potassium hydroxide and ethylene glycol at 180° C. The procedure of Mitchell *et al.* underwent considerable modifications culminating in the American Oil Chemists' Society Official Method Cd 7-58.³⁵ The development of the method in its present form has been described by O'Connor in his paper delivered before the American Oil Chemists' Society Short Course on Analytical Techniques at the University of Illinois in August, 1955.³⁶

The method was first proposed to determine linoleic and linolenic acids. It was shortly extended to include arachidonic acid by Brice and his co-workers, using absorptivities proposed by Beadle and Kraybill. It was later extended to include pentaenoic

acids by Herb and Riemenschneider and hexaenoic acids by Hammond and Lundberg. Several natural fats and oils exhibit absorption bands characteristic of dienoic conjugations at 232 millimicrons and of trienoic conjugation at 268 millimicrons. The so-called "performed" conjugation was believed to arise from accidental conjugation of linoleic and linolenic acids during the extraction or subsequent processing of the oil. The appearance of linolenic acid in vegetable oils such as cottonseed, peanut, sesame, etc., which from chemical analyses were not believed to contain this acid; or the appearance in drying oils, such as soybean and linseed, of traces of arachidonic acid, heretofore considered as a constituent of animal and fish oils only, were attributed to the superior sensitivity of the spectrophotometric methods.

O'Connor *et al.* demonstrated the oxidizability of both linoleic and linolenic acids to yield conjugation of the next higher order, i.e., trienoic from linoleic and tetraenoic from linolenic acids. Hilditch *et al.* questioned the validity of considering this "performed" conjugation as evidence for unsaturated fatty acids, and Swift *et al.* showed that it was, very probably the result of oxidation to produce alpha-, beta-unsaturated aldehydes and dienals which exhibit characteristic absorption at about these wavelengths. Swain and Brice made a detailed study of the formation of such constituents from which they were able to demonstrate that traces of "performed" conjugation absorption arise from autooxidation products of oleic, linoleic and linolenic acids. As a result of these investigations it is now well established that "performed" conjugation is more likely a measure of the autooxidation of an oil rather than evidence for conjugated fatty acids.

Several modifications have been made and are now incorporated into the AOCS official method to improve the precision and accuracy. O'Connor, Heinzelman, and Dollear,

using the method to determine soybean oil admixed with cottonseed oil by measuring the trienoic conjugation arising from the linolenic acid contents of the former only, proposed a complete nitrogen blanket both during the isomerization and during the preparation of the reagent in order to avoid oxidation of the readily oxidizable components. Brice and co-workers introduced mathematical equations to correct for "background" absorption when applying the method to very small quantities of linoleic, linolenic and arachidonic acids in animal fats and tallow. These corrections, while of considerable value when measuring small quantities, 1% or less, of the constituent acids, are not only unnecessary, but undesirable in the analysis of vegetable and drying oils where acid concentrations are of the order of 20 to 50%.

Hilditch and co-workers proposed two different conditions of alkali isomerization, one ideal for linoleic and the other for linolenic acids. White and Quackenbush³⁷ suggested a simplified isomerization procedure and Collins and Sedgwick³⁸ have described a simplification of the AOCS procedure which permits the routine analysis of 60 samples of soybean for linoleic and linolenic acids in a single day. Birch³⁹ has suggested the use of potassium amide in liquid ammonia as a stronger base for the alkali isomerization and Davenport *et al.*⁴⁰ have reported a preliminary investigation of the use of potassium *tert.*-butoxide in *tert.*-butanol. Sreenivasan and Brown⁴¹ have described in more detail the use of this reagent in the isomerization of linoleic and linolenic and other polyunsaturated acids and its application in the spectrophotometric estimation of these acids.

The introduction of a microtechnique by Herb and Riemenschneider has proved particularly useful in medical, biochemical and other applications where sample size is a serious problem.

Several discrepancies were reported in measurements of partially hydrogenated fats

and oil by the alkali isomerization—ultraviolet spectrophotometric method. Riemen-schneider and co-workers showed that the rate of isomerization and magnitude of the absorptivities differ for different *cis*, *cis*-, *cis*, *trans*-, and *trans*, *trans*-acids. Therefore the accuracy of the method, based on *cis*-acids only will not be satisfactory when samples such as partially hydrogenated materials (which can be shown by infrared absorption spectroscopy to contain a mixture of *cis*- and *trans*-acids) are analyzed. Brice and his co-workers argued that, while the oils examined contained fatty acids in the naturally occurring *cis*-form, the absorption constants used in the spectrophotometric calculations were derived from acids prepared by bromination-debromination methods, which produce a mixture of *cis*- and *trans*-isomers. They used pure *cis*-linoleic, linolenic and arachidonic acids, prepared by Riemen-schneider and co-workers, greatly improving the accuracy of the procedure. The method is not now considered applicable to the analysis of any sample which can be shown, by means of infrared absorption spectroscopy, to contain *trans*-isomers.

Brice *et al.* showed the excellent agreement which can be obtained by the spectrophotometric method when analyzing all *cis*-containing products and O'Connor *et al.* made a detailed comparison with the chemical methods for the analysis of a number of cottonseed oils and also showed good agreement. Baldwin and Longenecker tested the method by the analysis of known mixtures of purified methyl esters and Baldwin and Daubert with the analysis of synthetic glycerides. Firestone⁴² showed that the use of the method as proposed by Dugan and Petheram⁴³ and by Crouse and Leffler⁴⁴ for the determination of adulteration of ground beef, pork, or lamb, with horsemeat had been found satisfactory by the Association of Official Agricultural Chemists, who have adopted an official method very similar to that of the American Oil Chemists' Society.

Firestone⁴⁵ has also shown that the spectrophotometric method is ideal for the detection of soya oil adulteration of commercial corn oil and that butter fats can be satisfactorily distinguished from margarine fats. Beadle and co-workers have shown that lard can be detected in hydrogenated vegetable oils.

References to original papers describing extensions, improvements and application of the alkali isomerization ultraviolet absorption method will be found in the report by O'Connor.⁴⁶

Investigations of Oxidation by Means of Ultraviolet Absorption Spectroscopy

As mentioned earlier, there are exceptions to the rule that selective absorption arises from conjugated unsaturation. One of the most useful applications of low-magnitude selective absorption exhibited by non-conjugated unsaturated groups to investigations of fats and oils is that of the carbonyl linkage, C=O. This group in aldehydes or ketones, but not in acids or ethers, gives rise to a low broad characteristic band in the region between about 260 and 290 millimicrons. The appearance of such a band as fatty acids or derivatives undergo change, as evidenced by chemical measurements of viscosity, peroxide value, etc., indicates oxidation. Measurement of the intensities can be used to estimate the degree of oxidative reaction. When this group is conjugated to the ethylenic linkage —C=C—C=O , conjugated absorption in the diene, triene, tetraene, etc., regions is produced. Ultraviolet absorption studies of these groups have been very useful in investigations of autoxidation of vegetable oils, the drying processes of drying oils, the development of color in oils, and the factors affecting rancidity or keeping quality of oils.

Mitchell and Kraybill⁴⁶ showed that bleaching with fuller's earth gives rise to absorption bands in the spectra of vegetable oils. Oils containing linoleic acid develop

bands in the triene region, oils containing linoleic and linolenic acids in the triene and tetraene regions. These workers compared the ultraviolet absorption spectra of heat-bodied linseed oil (in vacuo at 307°C) and blown linseed (104.4°C). Both oils exhibited characteristic absorption in the diene region; only the blown oil exhibited characteristic bands in the triene region. Thus, by means of ultraviolet absorption spectra, it is possible to distinguish between linseed oil polymerized in vacuo and oxidized linseed oil in mixtures with raw linseed oil. The absorptivity at 232 millimicrons may be used for the quantitative analysis of oxidized or heat-bodied linseed oil in admixture with raw linseed oil.

O'Connor *et al.*, as pointed out earlier, demonstrated the readily oxidizable properties of both linoleic and linolenic acids to yield conjugation of the next higher order, i.e., trienoic from linoleic acid and tetraenoic from linolenic acids, and Swift *et al.* showed that oxidation of cottonseed oil gave rise to products identified as alpha- and beta-unsaturated aldehydes and dienals which exhibit characteristic absorption at these wavelengths. They attributed the selective absorption to conjugation of the carbonyl and ethylenic linkages. These experiments all indicated that oxidation is the primary cause of the formation of the conjugated systems and that ethylenic conjugation may follow oxidation and subsequent dehydration. This hypothesis was definitely confirmed by the detailed reinvestigation of formation of such constituents by Swain and Brice. Their work showed that the conjugated dienoic, trienoic and tetraenoic fatty acids encountered in the ultraviolet spectra of several alkali-isomerized vegetable oils have their origin in oxidation products of oleic, linoleic and linolenic acids. Holman and co-workers studied the ultraviolet absorption of pure and oxidized monoethenoic, octadecadienoic and octadecatrenoic acids

and esters and the products of lipoxidase oxidation of natural fats.

Wolff⁴⁷ has made several investigations of the oxidation of fatty acids and of natural oils by means of ultraviolet absorption. The ultraviolet absorption of pure linoleic acid and of almond, peanut, and olive oils increased with peroxide value. The oils also revealed an increased absorption at 270 millimicrons. Increased absorption at 232 millimicrons was attributed to hydroperoxide formation and that at 270 millimicrons as arising from ketonic oxidation, probably to produce diketones. Bleaching clay ("Clarsil") caused increased absorption at 270 millimicrons and a decrease at 232 millimicrons, interpreted as a decomposition of the hydroperoxide and the formation of more highly conjugated systems. Air oxidation of linseed oil, as investigated by ultraviolet absorption, indicated hydroperoxide formation at lower temperatures and decomposition to secondary oxidation products at higher temperatures. Ratios of the absorptivities at 232 and 270 millimicrons were suggested to: (a) differentiate stand oil from boiled oil; (b) estimate boiled oil in stand oil; and (c) distinguish extracted oil (which is heated to expel solvent) from raw pressed oil. Decolorizing earth increased absorption at 270 millimicrons and decreased it at 232 millimicrons, but at higher temperatures (150°) absorption at 303 and 317 millimicrons is produced without changing that at 232 or 270 millimicrons. Wolff showed that rancidity can be detected by ultraviolet spectrophotometry in linoleates; oleates and olive, peanut, and almond oils by the formation of conjugated double bonds.

Wolff⁴⁸ has published a review of the use of ultraviolet spectrophotometry in the examination of oils, fatty acids and refined materials for oxidation products, antioxidants and other components and has described the determination of antioxidants, butyl hydroxytoluene, butyl hydroxyanisole and gallates, in oils and lard.

Vaillant⁴⁹ also using ultraviolet spectrophotometry, showed, in a series of publications, that during initial stages of the standolization of linseed oil the linoleic acid disappears more rapidly than the linolenic acid. When the viscosity is 1 poise, linolenic acid disappears seven times as fast as linoleic acid, but above 60 poises, the velocity is the same for both acids. Minutilli⁵⁰ demonstrated, by means of a spectrophotometric examination of linseed oil during standolization, that the stand oils prepared in an inert gas atmosphere are of better quality than those prepared by heating in air. Ultraviolet absorption curves showed that heating in air produces conjugated diene constituents.

The potentialities of ultraviolet absorption as a tool for investigation of rancidification in fats has been summed up by Lundberg, Holman, and Burr.⁵¹ They concluded that preliminary investigations clearly demonstrated "that there is promise of much knowledge to be gained concerning the course and mechanism of the autoxidation of fats, at least in the early stages, through spectroscopic studies." Machulis⁵² demonstrated that while chemical methods and organoleptic evaluation permit detection of rancidity of fats only when the process has reached a stage at which the fat is practically inedible, ultraviolet absorption spectroscopy is more sensitive and more objective, evaluating incipient stages of rancidity on the basis of decreased transmittancy, particularly at 280 millimicrons.

Hendrickson, Cox, and Konen⁵³ reporting on the applications of ultraviolet spectrophotometry in drying oil research concluded that this technique "is a valuable tool for investigation of some of the chemical changes which occur as a vegetable oil film dries and ages." A review of the applications of ultraviolet absorption spectra to drying oil chemistry has been published by Kass⁵⁴ and Ahlers⁵⁵ has published surveys of the applications of ultraviolet absorption in oils and resins and in paint research. Wolff⁵⁶ has

reviewed spectrophotometric methods for the determination of degree of alteration in his articles entitled "Present Knowledge About the Alteration of Fats," and "Physical-Chemical Methods of Analysis of Fatty Materials and Their Derivatives."

Japanese workers have reported several studied on the oxidation of fatty acids, particularly higher polyunsaturated acids, by means of ultraviolet spectrophotometry. An excellent article by Toyama⁵⁷ is a review, in English, compiled from several papers published in Japanese by this worker and his colleagues.

Miscellaneous Ultraviolet Absorption Studies of Vegetable and Drying Oils

O'Connor *et al.*⁵⁸ examined the ultraviolet spectra of several vegetable and drying oils. They correlated the significant absorption bands occurring in these spectra with compounds giving rise to them and interpreted modifications in absorption bands which accompany various types of extractions and with chemical changes which occur during refining, bleaching and deodorizing. Tsuchiya and Kaneko⁵⁹ studied, in a similar manner, the ultraviolet spectra of several oils of Japan and discussed bands which appear in the spectra of these less common oils. Hires and Tombacz and Franzke⁶⁰ have reviewed the applications of ultraviolet spectra to vegetable oils and to natural vegetable fats, respectively. Minutilli⁶¹ has published a review entitled "Application of Spectrophotometry in the Study of Vegetable Oils," and Uzzan⁶² has shown the advantages of the use of ultraviolet absorption spectra in studies of olive oils.

Although colorimetric methods have been widely employed to detect adulteration of olive oils, ultraviolet absorption spectroscopy is also being used for this purpose. Montefredine and La Porta⁶³ have published a detailed review of the applications of spectrophotometry to the analysis of olive oils.

They tabulated data from 206 samples of olive oil and showed that ratios of the absorptivities at 232 millimicrons to those at 270 millimicrons are generally higher than 10 and may reach 20 for "superfine" olive oils. Fabbietti⁶⁴ showed that ratios of absorptivities at eight wavelengths in the spectra of olive oils subjected to Liebermann's reaction yield criteria of quality and purity of the oil. If the ratio at 460 millimicrons/365 millimicrons is less than 1, the oil is probably not a virgin olive oil or is olive oil subjected to refining process "A," or is a mixture of these two. If 0.8 or less there is no doubt. If greater than 1, the oil can be a super refined virgin olive oil, a good grade oil, or a process "A" refined oil, or a mixture of the three. If the ratio of absorptivities at 420 millimicrons to 400 millimicrons is less than 0.95, the oil has probably been adulterated by process "B" refined oil or by animal or vegetable oil. A ratio 610 millimicrons/500 millimicrons less than 0.90 indicates that fractionated or esterified animal oil has been added, while greater than 1.23 indicates the presence of corn oil. The ratio of absorptivities at 670 millimicrons to 620 millimicrons greater than 1.10 indicates a superfine virgin olive oil. Ninnis and Barbili⁶⁵ used ultraviolet absorption in the examination of 20 Greek olive oils to detect adulteration by refined and rancid oils and vegetable products. Mattei and Volpi⁶⁶ used ratios of absorbence at 232 to 270 millimicrons to distinguish virgin olive oils from oils refined by the two processes and to detect small percentages of refined oils in virgin oils. This ratio, they report, will not detect adulteration of esterified oil with animal oleins, nor distinguish an oil refined by alkali or esterification. Foschini and Minutilli⁶⁷ and Minutilli⁶⁸ demonstrated that fatty acids and unsaponifiable matter from refined (earth-bleached) olive oils showed characteristic absorption at 260 and 280 millimicrons not observed in the spectra of natural olive oils and that the peak at 269 millimicrons, at-

tributed to conjugated triene, becomes more prominent during deodorizing and decolorizing.

REFERENCES

1. Methods of Vitamin Assay, Association of Vitamin Chemists, Inc., 2nd ed. Intersciences Publishers, Inc., New York, (1951).
2. MELNICK, DANIEL I., LUCKMANN, FREDERICK H., AND VAHLTEICH, HANS W., Estimation of Vitamin A in Margarine, *J. Am. Oil Chemists' Soc.*, **29**, 104-8 (1952); II. LUCKMANN, FREDERICK H., MELNICK, DANIEL, AND VAHLTEICH, HANS W., *Ibid*; 121-6; III. LUCKMANN, FREDERICK H., GOODING, CHESTER M., MELNICK, DANIEL, AND VAHLTEICH, HANS W., *Ibid*; 321-30.
3. MURRAY, M. D., O'CONNOR, R. T., SUAREZ C., CARLOS, AND BICKFORD, W. G., Sesame Oil. X. The Stability of Vitamin A in Sesame Oil and in Margarine Stock Containing Sesame Oil, *J. Am. Oil Chemists' Soc.*, **30**, 329-31 (1953).
- 4A. MORTON, R. A., AND STUBBS, A. L., Photoelectric Spectrophotometry Applied to the Analysis of Mixtures and Vitamin Oils, *Analyst*, **71**, 348-56 (1946); 4B. Reexamination of Halibut-Liver Oil. Relation Between Biological Potency and Ultraviolet Absorption Due to Vitamin A, *Biochem. J.*, **41**, 525-29 (1947); 4C. Studies in Vitamin A. Spectrophotometric Determination of Vitamin A in Liver Oil. Correction for Irrelevant Absorption, *Ibid*, **42**, 195-203 (1948).
5. BRAEKKAN, O. R., AND LAMBERTSEN, GEORG, Determination of Vitamin A in Cod Liver Oil and Vitamin Oils, *Fiskeridirektoratets. Skrifter Ser. Teknol. Undersokelser*, **2**, No. 9, 1-20 (1952).
6. "Pharmacopeia of the United States," 15th rev. pp 941-2 (1955), Mack Printing Co., Easton, Pa., (1955).
7. HALVORSON, H. A., GRIFFIN, E. L., AND SMITH, J. B., Report of Subcommittee A on Report of Referees, *J. Assoc. Off. Agr. Chemists*, **33**, 43 (1950).
- 8A. WILKIE, J. B., Report on Vitamin A. The Present Status of the Chromatographic Spectrophotometric Procedure for the Estimation of Vitamin A in Margarine, *J. Assoc. Off. Agr. Chemists*, **30**, 382-91 (1947); 8B. Report on Vitamin A. Further Comparison of the Spectrophotometric and Antimony Trichloride Methods for Vitamin A in Margarine, *Ibid*; **32**, 455-9 (1949).

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9. ROSNER, L., AND KAN, HENRIETTA, Chromatographic-Spectrophotometric Method for Determination of Vitamin A in Margarine, *J. Assoc. Off. Agr. Chemists*, **37**, 887-94, (1954).
10. BOLDINGH, J., AND DROST, J. R., The Determination of Vitamin A in Margarine, *J. Am. Oil Chemists' Soc.*, **28**, 480-3 (1951).
11. BRÆKKAN, O. R., AND LAMBERTSEN, GEORG, Determination of Vitamin A in Margarine, *Tids. Kjemi. Bergvesen Met.*, **12**, 29-31 (1952).
- 12A. LORD, J. W., AND BRADLEY, P. M., Modified Method for the Spectrophotometric Determination of Vitamin A in Margarine, *Analyst*, **80**, 429-38 (1955); 12B. TAYLOR, R. J., Discussion, *Ibid.*, 438-441.
- 13A. WILKIE, J. B., AND JONES, S. W., Standardization of Alumina Adsorbents for Vitamin A Chromatography, *J. Assoc. Off. Agr. Chemists*, **37**, 880-7 (1954); 13B. WILKIE, J. B., AND JONES, S. W., Standardization of Adsorbent Mixtures Used in Vitamin A Chromatography, *Anal. Chem.*, **24**, 1409-11 (1952).
14. FRIEDMAN, LEO, Vitamin A in Oleomargarine, *J. Assoc. Off. Agr. Chemists*, **43**, 6-14 (1960).
15. MORTON, R. A., AND BRO-RASMUSSEN, F., Comments on the Determination of Vitamin A in Natural Products and Especially Cod-Liver Oils, *Analyst*, **80**, 410-8 (1955).
16. BRO-RASMUSSEN, F., HJARDE, W., AND POROTNIKOFF, OLGA, Chromatographic Separation of Vitamin A-Active Compounds in Cod-Liver Oil, *Analyst*, **80**, 418-28 (1955).
17. TSUCHIYA, TOMOTARO, AND KANEKO, RYOHEI, Oils and Fats in Japan. V. Ultraviolet Absorption Spectra, *Repts. Govt. Chem. Ind. Research Inst. (Tokyo)*, **49**, 141-5 (1954); *J. Chem. Soc., Japan, Ind. Chem. Sect.*, **56**, 295-7 (1953).
18. KAMATH, G. G., AND MAGAR, N. G., Ultraviolet Absorption Characteristics of Some Indian Shark-Liver Oils, *Indian J. Med. Research*, **41**, 339-47 (1953).
- 19A. BROCKMANN, H., The Isolation of Antirachitic Vitamin from Tuna Fish Liver Oil, *Z. Physiol. Chem.*, **241**, 104-15 (1936); 19B. BROCKMANN, H., AND BUSSE, A., The Antirachitic Vitamin of Blue Fin Tuna Liver Oil, *Ibid.*: **256**, 252-70 (1938); 19C. BROCKMANN, H., AND BUSSE, A., Crystalline Vitamin D from Tuna Fish Liver Oil, *Naturwiss.*, **26**, 122-3 (1938).
20. REERINK, E. H., VAN WIJKE, A., AND VAN NIEKERK, J., Physical Methods of Vitamin Investigation, *Chem. Weekblad*, **29**, 645-50 (1932).
21. TÖPELMANN, H., AND SCHUEKNECHT, W., Spectroscopic Evidence of Vitamin D in Wool-Fat Preparations, *Z. Vitaminforsch.*, **4**, 111-20 (1935).
22. OL'KHIN, S. B., Spectral Analysis of Some Vitamin D Preparations, *Proc. Sci. Inst. Vitamin Research, U.S.S.R.*, **3**, No. 1, 28-9 (1941).
23. MARCUSSEN, E., Quantitative Chromatographical Isolation and Spectrographical Determination of Vitamin D from Liver Oils, *Densk Tids. Farm.*, **13**, 141-59 (1939).
- 24A. EWING, D. T., SCHLABACH, T. D., POWELL, M. J., VAITEKUS, J. W., AND BIRD, O. D., Spectrophotometric Determination of Vitamin D in Presence of Vitamin A, *Anal. Chem.*, **26**, 1406-9 (1954); 24B. EWING, D. T., KINGSLEY, G. V., BROWN, R. A., AND EMMETT, A. D., Physical Chemical Methods for Determination of Vitamins D in Fish Liver Oils, *Ind. Eng. Chem. (Anal. Ed.)*, **15**, 301-5 (1943).
25. PASCHKE, R. F., TOLBERG, W., AND WHEELER, D. H., Cis, Trans Isomerization of Eleostearate Isomers, *J. Am. Oil Chemists' Soc.*, **30**, 97-9 (1953).
26. BICKFORD, W. G., DUPRE', E. F., MACK, C. H., AND O'CONNOR, R. T., The Infrared Spectra and the Structural Relationship Between Alpha- and Beta-Eleostearic Acids and Their Maleic Anhydride Adducts, *J. Am. Oil Chemists' Soc.*, **30**, 376-81 (1953).
27. O'CONNOR, R. T., HEINZELMAN, D. C., FREEMAN, A. F., AND PACK, F. C., Spectrophotometric Determination of Alpha-Eleostearic Acid in Freshly Extracted Tung Oil, *Ind. Eng. Chem. (Anal. Ed.)*, **17**, 467-70 (1945).
28. HOFFMAN, J. S., O'CONNOR, R. T., HEINZELMAN, D. C., AND BICKFORD, W. G., A Simplified Method for the Preparation of Alpha- and Beta-Eleostearic Acids and a Revised Spectrophotometric Procedure for their Determination, *J. Am. Oil Chemists' Soc.*, **34**, 338-42 (1957).
- 29A. BUDOWSKI, PIERRE, O'CONNOR, R. T., AND FIELD, E. T., Sesame Oil IV. Determination of Free and Bound Sesamol, *J. Am. Oil Chemists' Soc.*, **27**, 307-10 (1950).
- 29B. Sesame Oil VI. Determination of Sesamin, *Ibid.*; **28**, 51-4 (1951).
30. SUAREZ C., CARLOS, O'CONNOR, R. T., FIELD, E. T., AND BICKFORD, W. G., Determination of Sesamol, Sesamolin and Sesamin in Sesamin Concentrates and Oils, *Anal. Chem.*, **24**, 668-71 (1952).
31. BEROZA, MORTON, Determination of Sesamol, Sesamolin, and Sesamin, *Anal. Chem.*, **26**, 1173-6 (1954).

32. MITCHELL, J. H., JR., KRATBILL, H. R., AND ZSCHILLE, F. P. Quantitative Spectral Analysis of Fats, *Ind. Eng. Chem. (Anal. Ed.)*, **15**, 1-3 (1943).
- 33A. DANN, W. J., AND MOORE, T., The Absorption Spectra of the Mixed Fatty Acids from Cod-Liver Oil, *Biochem. J.*, **27**, 1166-9 (1933); 33B. MOORE, T., Spectroscopic Changes in Fatty Acids, I. Changes in the Absorption Spectra of Various Fats Induced by Treatment with Potassium Hydroxide, *Ibid.*; **31**, 138-54 (1937); 33C. MOORE, T., Spectroscopic Changes in Fatty Acids. VI. General, *Ibid.*; **33**, 1635-8 (1939).
34. KASS, J. P., MILLER, E. S., AND BURR, G. O., A Note on the Constitution of Linoleyl Alcohol Prepared by Sodium Reduction of Linoleic Acid, *J. Am. Chem. Soc.*, **61**, 482-3 (1939).
35. MEHLENBACHER, V. C., HOPPER, T. H., AND SALLER, E. W., Eds., Official and Tentative Methods, American Oil Chemists' Society, 2nd Ed., American Oil Chemists' Soc., Chicago, Ill., (1959).
36. O'CONNOR, ROBERT T., Ultraviolet Absorption Spectroscopy, *J. Am. Oil Chemists' Soc.*, **32**, 616-24 (1955).
37. WHITE, HAROLD B., JR., AND QUACKENBUSH, F. W., A Simplified Technique for Analysis by Alkali Isomerization, *J. Am. Oil Chemists' Soc.*, **36**, 653-6 (1959).
38. COLLINS, F. I., AND SEDGWICK, V. E., A Rapid Spectrophotometric Method of Determining Linoleic and Linolenic Acid Components in Soybean Oils, *J. Am. Oil Chemists' Soc.*, **33**, 149-52 (1956).
39. BIRCH, A. J., The Reduction of Organic Compounds by Metal Ammonium Solutions, *Quart. Rev. (London)*, **4**, 69-93 (1950).
40. DAVENPORT, J. B., BIRCH, A. J., AND RYAN, A. J., The Alkali-Catalyzed Isomerization of Unsaturated Compounds, *Chemistry and Industry* (1956), 136-7.
- 41A. SREENIVASAN, B. S., AND BROWN, J. B., Isomerization of Linoleic and Linolenic and other Polyunsaturated Acids with Potassium Tertiary Butoxide and its Application in the Spectrophotometric Estimation of these Acids, *J. Am. Oil Chemists' Soc.*, **33**, 521-6 (1956); 41B. Further Studies on the Isomerization of Polyunsaturated Fatty Acids by Potassium Tertiary Butoxide, *Ibid.*; **35**, 89-93 (1958).
42. FIRESTONE, DAVID, Report on Spectrophotometric Method for Fats and Oils, *J. Assoc. Off. Agr. Chemists*, **37**, 833-42 (1954).
43. DUGAN, L. R., JR., AND PETHERAM, M., A Study of the Determination of Horse Fat in the Presence of Pork and Beef Fats, *J. Assoc. Off. Agr. Chemists*, **35**, 767-71 (1952).
44. CROUSE, R. H., AND LEFFLER, I. D., Determination of Horsemeat in Meat Products by a Modified Paschke Method, *Food Research*, **18**, 253-60 (1953).
45. FIRESTONE, DAVID, Report on Spectrophotometric Method for Fats and Oils, *J. Assoc. Off. Agr. Chemists*, **38**, 657-63 (1955).
- 46A. MITCHELL, J. H., JR., AND KRATBILL, H. R., Formation of Conjugated Material During Bleaching of Vegetable Oils, *J. Am. Chem. Soc.*, **64**, 988-94 (1942); 46B. Ultraviolet Absorption Spectra of Linseed Oil, *Ind. Eng. Chem. (Anal. Ed.)*, **13**, 765-8 (1941).
- 47A. WOLFF, J. P., Spectrophotometric Study of Rancidity in Oils, *Rev. Franc. Crops Gras*, **1**, 214-26 (1954), 330-8 (1954); 47B. WOLFF, J. P., Ultraviolet Spectrophotometry of the Oxidation of Linseed Oil, *Peintures, Pigments, Vernis*, **31**, 612-7 (1955); 47C. WOLFF, J. P., Spectrophotometric Study of Rancidity in Oils, *Parfumerie mod.*, **46**, 53-61 (1954).
- 48A. WOLFF, J. P., Use of Visible and Ultraviolet Spectrophotometry in Industries Concerned with Fatty Materials and their Derivatives, *Chem. Anal.*, **40**, 159-66 (1958); 48B. WOLFF, J. P., Application of Ultraviolet Spectrophotometry to the Determination of Some Antioxidants, *Rev. Franc. Crops Gras*, **5**, 630-40 (1958).
49. VAILLANT, H., Analytical Study of Polymerized Linseed Oil, *Rev. Franc. Crops Gras*, **2**, 21-7; 159-65; 394-405 (1955).
50. MINUTILLI, F., Spectrophotometric Examination of Linseed Oil During Standolization in an Inert Gas Atmosphere. *Olii Minerali, Grasse e Saponi Colori e Vernici*, **35**, 2-3 (1958).
51. LUNDBERG, W. O., HOLMAN, R. T., AND BURR, G. O., Spectroscopic Changes in Fats During Rancidification, *Oil and Soap*, **23**, 10-14 (1946).
52. MACHULIS, P., Determination of Rancidity of Linseed Oil by Spectrophotometric Method, *Uchenye Zapiski Vil'nyus. Univ., Ser. Mat. Fiz. I Khim. Nauk*, (1956) No. 6, 83-91.
53. HENDRICKSON, M. J., COX, R. P., AND KONEN, J. C., Some Applications of Ultraviolet Spectrophotometry in Drying Oil Research, *J. Am. Oil Chemists' Soc.*, **25**, 73-7 (1948).
54. KASS, J. P., in Ultraviolet Absorption Studies of Drying Oils, Protective and Decorative Coatings, ed. by J. J. Matiello, Vol. 4, chp.

- 12, John Wiley and Sons, Inc., New York, (1944).
- 55A. AHLERS, N. H. E., The Structure of Oils and Resins: Spectroscopy, *J. Oil & Colour Chemists' Assoc.*, **37**, 533-61 (1954); 55B. Absorption Spectroscopy in Paint Research—A Survey, *Ibid.*, **33**, 421-51 (1950).
- 56A. WOLFF, J. P., Present Knowledge about the Alteration of Fats, *Rev. Franc. Crops Gras.*, **6**, 275-88 (1959); 56B. WOLFF, J. P. Physical Chemical Methods of Analysis of Fatty Materials and Their Derivatives, *Inds. Aliment, et agr. (Paris)*, **75**, 639-48 (1958).
57. TOYAMA, YOSHIYUKI, The Oxidation of Unsaturated Fatty Acids, *Mem. Fac. Eng., Nagoya Univ.*, **4**, 121-46 (1952).
- 58A. O'CONNOR, ROBERT T., FIELD, ELSIE T., JEFFERSON, M. E., AND DOLLEAR, F. G., The Influence of Processing on the Spectral Properties of Vegetable Oils, *J. Am. Oil Chemists' Soc.*, **26**, 710-18 (1949); 58B. O'CONNOR, ROBERT T., POMINSKI, C. H., HEINZELMAN, D. C., HOWELL, HILDA, AND VON DER HAAR, PATRICIA, Influence of Condition of Seed on the Spectral Properties of Crude and Processed Hydraulic Cottonseed Oils, *J. Am. Oil Chemists' Soc.*, **29**, 220-24 (1952).
59. TSUCHIYA, TOMOTARO, AND KANEKO, RYOHEI, Oils and Fats in Japan. V. Ultraviolet Absorption Spectra, *Repts. Govt. Chem. Ind. Research Inst. (Tokyo)*, **49**, 141-5 (1954).
- 60A. HIRSH, J., AND TOMBACZ, E., Ultraviolet Absorption Spectra Studies of Vegetable Oils, *Magyar Kem. Folyóirat*, **59**, 1-5 (1953); 60B. FRANZKE, CL., Ultraviolet Absorption Spectra of Natural Vegetable Fats, *Nahrung*, **2**, 639-54 (1958).
61. MINUTILLI, F., Application of Spectrophotometry in the Study of Vegetable Oils, *Rass. Chim.*, **10**, (3), 24-7 (1958).
62. UZZAN, A., Spectrophotometric Study of Olive Oils in the Ultraviolet Region, *Rev. Franc. Crops Gras.*, **3**, 9-17 (1956).
63. MONTEFREDINE, A., AND LA PORTA, L., Applications of Spectrophotometry to the Analysis of Olive Oils. I. The Use of the Ultraviolet Spectrophotometer for the Identification of the Superfine Olive Oils, *Olii Minerali, Grassi e Saponi, Colori e Vernici*, **36**, 31-6 and 64-72 (1959).
64. FABBRIETI, A., Spectrophotometric Examination of Olive Oils, *Boll. Lab. Chim. Provinciali (Bologna)*, **9**, 287-96 (1958).
65. NINNIS, L., AND BARBILI, M., Ultraviolet Spectrum of Greek Olive Oils, *Prakt. Akad. Athenon*, **31**, 97-108 (1956).
66. MATTEI, R., AND VOLPI, G., Ultraviolet Spectrographic Characteristics of Italian Olive Oils, with Special Reference to Those Mixed with Refined or Extraneous Oils, *Olearia*, **13**, 55-61 (1959).
67. FOSCHINI, A., AND MINUTILLI, F., Effect of Refining on Ultraviolet Absorption of Olive Oil, *Rass. Chim.*, **9** (4) 10-12 (1957).
68. MINUTILLI, F., Spectrophotometric Study of Olive Oils, *Rass. Chim.*, **11**(5) 14-16 (1957).

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FUSED SALTS SPECTROPHOTOMETRY

Fused salts play important roles in many areas of nuclear technology. These include high temperature homogeneous reactors, fuel processing systems, and the production of very pure metals like uranium and thorium. There is little doubt that, in the future, fused salts will find still other applications in the nuclear energy field.

A better understanding of the chemistry of fused salts is required in order to meet successfully the many challenging problems associated with the present and possible future uses of these versatile materials.

Although fused salts constitute the largest class of nonaqueous inorganic solvents, chemical reactions are virtually unexplored in these media. The development of a solution chemistry in fused salts will depend very largely on knowledge concerning the oxidation states and oxidation-reduction behavior of the solute ions. Information about the kinds and stabilities of complex ions present in these solvents is equally important because of the profound effects such complexes may have on the oxidation-reduction potentials. The search for an experimental approach to these problems, led to the development of spectrophotometric measurements on fused salts principally by D. M. Gruen and associates at the Argonne National Laboratory,¹ B. Sundheim and students at New York University^{2a} and P. Smith and C. R. Boston at Oak Ridge National Laboratory.^{2a}

Absorption spectrophotometry has been

one of the classic tools in elucidating the chemistry of aqueous solutions. The recent application of this technique to studies of oxidation states and complex-ion formation in fused salts appears to make it a method of equal promise for exploring the chemistry of these nonaqueous solvents.^{2, 3}

Instrumentation. A general problem to be encountered in making spectrophotometric measurements at temperatures above 500°C is due to the emission of black body radiation from the sample and container.

This problem is serious at higher temperatures because in most commercially available spectrophotometers, light from the source passes first through the monochromator, then through the sample before finally striking the phototube. In these instruments therefore the phototube "sees" all of the black body radiation from the hot sample, in addition to the monochromatized beam. The signal (monochromatized beam) to noise (black body radiation) ratio rapidly diminishes with increasing temperature and is ap-

parently low enough at 550°C to make quantitative spectrophotometric measurements difficult.⁴

The solution to this problem was the simple expedient of reversing the positions of light housing and phototube. With this arrangement, both the light from the source and the black body radiation from the sample pass through the monochromator before striking the phototube. Thus, the black body radiation problem is overcome until the sample temperature approaches the light source temperature. The Beckman DU spectrophotometer was used in the published work of Gruen *et al.* since fortunately it is designed so that repositioning of the light source and detector is very easily accomplished.

The usual Beckman cell compartment was replaced by a water-cooled box which could be flushed with an inert gas during experiments. The block was machined to accommodate two 1 cm optical cells and was equipped with a handle for moving first one cell and then the other into the light

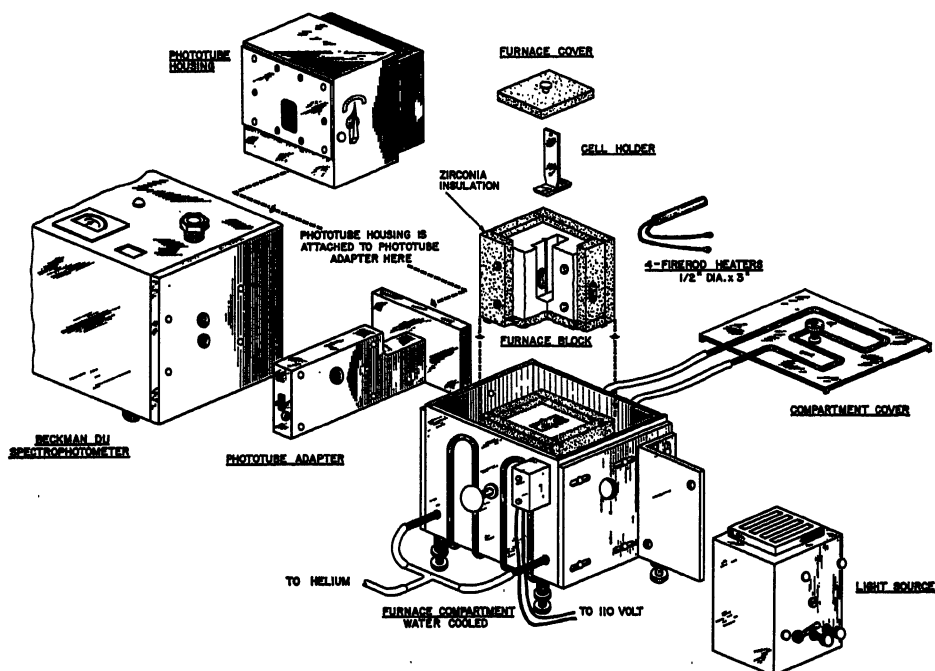


FIG. 1. Beckman "DU" spectrophotometer adapted for high-temperature measurements.

path. Holes sunk horizontally into the block held four "Firerod" $\frac{1}{2}$ in. heaters. The sides were insulated with $\frac{1}{2}$ in. zirconia plates.

Temperature control to $\pm 1^\circ$ was achieved with an electronic thermocouple control circuit and temperatures were measured with a thermocouple in close proximity of the sample.

Absorption spectra were obtained with this apparatus in the range 300–1200 $m\mu$ and from 150 to 850°C, the maximum attainable temperature.

Preparation of Samples. Much of the work thus far published has been done with solutions of actinide and other metal ions dissolved in anhydrous LiCl-KCl eutectic (59 mole % LiCl, m.p. 352°C).^{5, 6}

Rectangular quartz cells with a 10 mm light path were used for the optical work by Gruen in typical experiments. A blank cell was filled with eutectic alone by melting approximately 8 g of eutectic pellets. The sample cell was filled in exactly the same manner as the blank cell except that an appropriate quantity (1–100 mg) of the desired actinide or other transition metal halide was placed in the cell first.

After the spectra had been obtained, the cell was removed from the spectrophotometer and turned upside down to transfer the solution to the remaining circular section of quartz tubing which now served as a storage compartment. There the melt was allowed to solidify. To carry out analyses, the storage section was broken off from the cell proper and the salt column which in general was free of the surrounding walls, extracted from it.

Analyses were made either radiometrically as with Np, Pu, and Am or by more conventional methods as with U. Since the densities of the LiCl-KCl melts (density = 1.69 g/ml at 400°C) had been determined earlier as a function of temperature, the results of the analyses were expressed as moles of metal ion/liter of solution. The spectro-

photometric data were converted to molar extinction coefficients. With the data in this form, a direct comparison with aqueous solution spectra can be made.

Spectrophotometric measurements also are reported on solutions of transition metal ions in fused LiNO₃-KNO₃ eutectic (43 mole % LiNO₃, m.p. 132°C, density = 1.94 g/ml at 160°C) and in fused pyridinium chloride (m.p. 144.5°C, density = 1.14 g/ml at 160°C). Traces of moisture appeared not to be troublesome with these solvents at temperatures of 150–250°C where measurements were made. Consequently, the cells were left open to the atmosphere during an experiment. Standard 10 mm "Corex" absorption cells were used in this work.

Oxidation States of Metal Ions in Fused Salts

The spectrophotometric method for the determination of oxidation states depends on the fact that in general each oxidation state of a metal ion is characterized by a unique absorption spectrum. Of all the metal ions, the transition metal ions display the greatest multiplicity of oxidation states and are therefore of most interest from the point of view of this study.

Almost without exception the transition metal ions, that is the ions with partially filled d or f electron shells, possess absorption bands in the region 3000–12,000 Å which are due to electronic transitions.

These absorption bands have been very thoroughly studied by a large number of investigators. They are by now well known for most transition metal ions in a variety of oxidation states and in many different kinds of aqueous solutions and in crystals. The existence of this vast body of information has made possible the interpretation of the results on fused salts. The absorption spectra and oxidation states of a number of transition metal ions have been determined in this way.²

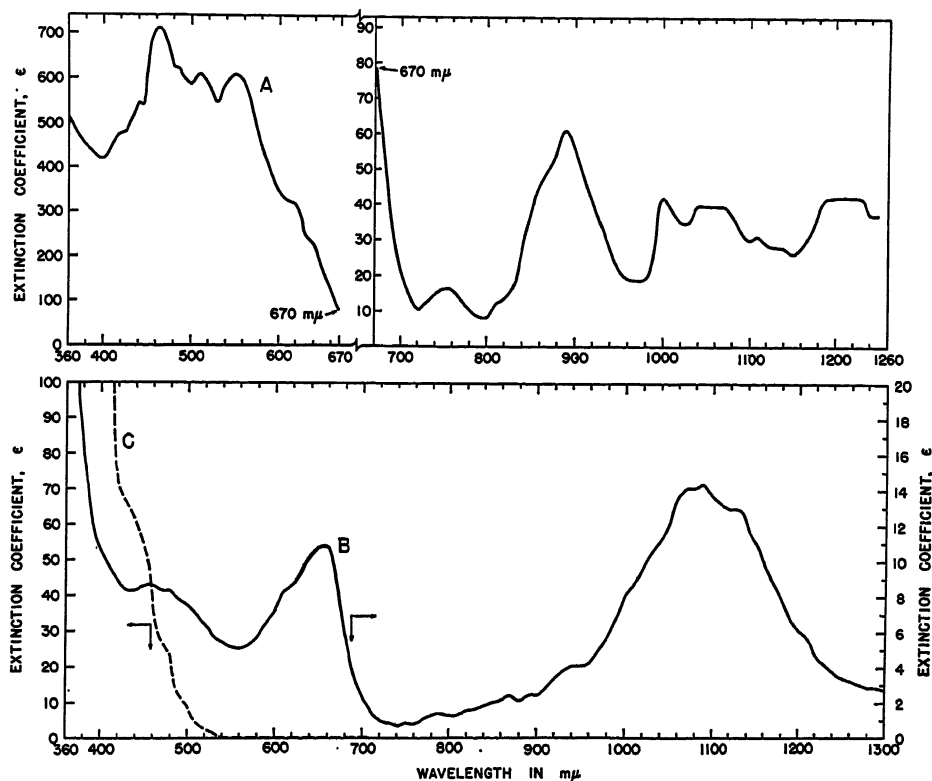


Fig. 2. Absorption spectra of uranium in various oxidation states in LiCl-KCl eutectic at 400°C.

Curve A: U(III)

Curve B: U(IV)

Curve C: U(VI)

Solutions in LiCl-KCl Eutectic. Only a few typical examples of spectrophotometric measurements reported in published work will illustrate the scope, indicative of continuing progress up to the present moment. Initially, solutions of U and Np in the (IV) oxidation state in LiCl-KCl eutectic were prepared in the Gruen work by dissolving UF_4 , UCl_4 or $^{237}NpCl_4$.

It was found possible to reduce both the U(IV) and the Np(IV) solutions chemically by reaction with Al metal.^{3a} In the case of the U(IV) solutions, U metal was also used as a reductant. The U(IV) solutions are green resembling aqueous solutions of tetravalent uranium. On reduction to the (III) state, the color changes to burgundy, reminiscent

of the color of aqueous solutions of trivalent uranium.^{13, 14} Np(IV) and Np(III) solutions in LiCl-KCl eutectic are yellow. Visually, the color change on reduction is difficult to detect. However, the absorption spectra, show conclusively that one is dealing with the (IV) and (III) oxidation states of Np.¹⁸

Oxidation of U(IV) to U(VI) and of Np(IV) to Np(V) was accomplished by reaction either with KNO_3 or by bubbling HCl gas through the solutions while they were exposed to the atmosphere. Visually, U(VI) and Np(V) solutions in LiCl-KCl eutectic are yellow and green respectively and resemble in this way the colors of aqueous solutions of these oxidation states. In all cases the absorption spectra were

similar to those for known oxidation states of these elements in aqueous solutions. For example, the U(IV) spectrum is characterized by a number of rather broad bands throughout the visible and near infrared region of the spectrum. These bands although much broader and lacking in structural detail occur at approximately the same wavelengths as do the major bands in crystals of the compounds Cs_2UCl_6 and $[(\text{CH}_3)_4\text{N}]_2\text{UCl}_6$ which were studied some time ago.^{7, 8} Spectra of solutions of UCl_4 in fused pyridinium chloride taken at 160°C show somewhat greater structural detail than the LiCl-KCl eutectic spectra presumably because these measurements can be made at lower temperatures.^{3a}

In the compounds Cs_2UCl_6 , and $[(\text{CH}_3)_4\text{N}]_2\text{UCl}_6$, the uranium is surrounded by six chloride ions in an almost regular octahedral configuration.⁹⁻¹¹ The similarity of the U(IV) spectrum in chloride melts with the single crystal spectra is evidence for the existence of UCl_6^- complex ions in the melts.

The extinction coefficients of the U(IV)

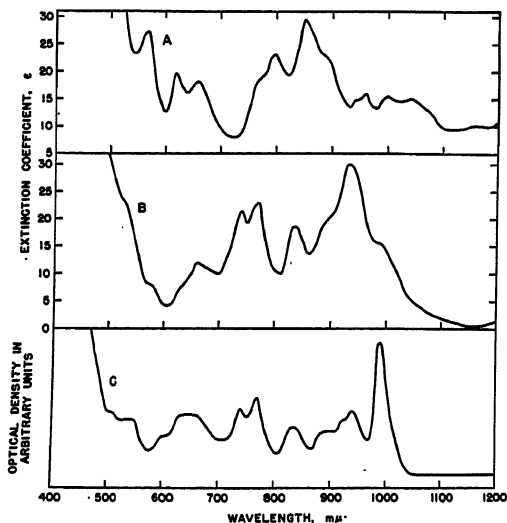


Fig. 3. Absorption spectra of neptunium in various oxidation states in LiCl-KCl eutectic.

Curve A: Np(III) at 600°C
 Curve B: Np(IV) at 600°C
 Curve C: Np(V) at 600°C

bands in LiCl-KCl eutectic are lower by a factor of about five compared to U(IV) spectra in aqueous solution.¹²

Corresponding results for plutonium and americium in both fused LiCl-KCl and $\text{LiNO}_3\text{-KNO}_3$ eutectics are reported in a recent paper.^{15a}

Solutions in $\text{LiNO}_3\text{-KNO}_3$ Eutectic.

From the point of view of oxidation-reduction reactions, the LiCl-KCl eutectic solvent served as an inert matrix for solutions of the actinide ions. It was to be expected that nitrate melts would exhibit oxidizing properties, with nitrate ions acting as oxide ion donors in the presence of strong oxide ion acceptors like U(IV), Np(IV) and Pu(III). However, nothing was known about the extent to which reactions of this sort would occur and indeed what oxidation state or mixture of oxidation states would be obtained. The spectrophotometric method can shed considerable light on these questions and emerges as an excellent way of studying oxide ion donor-acceptor relationships in fused salts.

Solutions in $\text{LiNO}_3\text{-KNO}_3$ eutectic were obtained by dissolving milligram quantities of UCl_4 , $^{237}\text{NpCl}_4$, $^{239}\text{PuCl}_3$ and $^{242}\text{AmCl}_3$. These solutions were examined spectrophotometrically.

Dissolution of UCl_4 in $\text{LiNO}_3\text{-KNO}_3$ eutectic results in complete oxidation to U(VI).^{3a} The spectrum of the yellow solution consists, except for the ultraviolet continuum, of a single smooth band with maximum at 430 mμ and with molar extinction coefficient equal to 31. This band is similar with respect to the half-width and the position of its maximum to the UO_2^{2+} band in aqueous acidic solution.¹⁶

Dissolution of NpCl_4 in $\text{LiNO}_3\text{-KNO}_3$ eutectic gives a green solution the spectrum of which is almost identical with that of Np(V) aqueous solution spectra.¹⁵

When PuCl_3 is placed in $\text{LiNO}_3\text{-KNO}_3$ eutectic, a precipitate is formed. The nature of the precipitate is not yet known. It is prob-

ably an oxynitrite or oxynitrate of Pu(IV). (In this respect, the behavior of PuCl_3 is similar to that of ThCl_4 . The latter compound has also been found to react with $\text{LiNO}_3\text{-KNO}_3$ eutectic to give an insoluble precipitate of unknown composition.) Not all of the Pu precipitates however. The spectrum of the solution is essentially identical with that of Pu(VI) in aqueous media.¹⁷

The behavior of Pu in the nitrate melt may imply that the first step in the oxidation process is to an intermediate Pu(V) state which then disproportionates to give Pu(IV) and Pu(VI).

Dissolution of AmCl_3 in $\text{LiNO}_3\text{-KNO}_3$ eutectic gives a pink solution the spectrum of which is very similar to that of Am(III) in aqueous solution.¹⁸

General Remarks Concerning the Oxidation States and Absorption Spectra of the Actinides in Fused Salts. In inert fused salt solvents like the alkali and alkaline earth halides, the actinides apparently can display the full spectrum of oxidation states known for aqueous solutions of these ions. In addition, because of the great resistance of these fused salt solvents to oxidation and reduction, unusual oxidation states like Th(II) and Am(II) which are not known in aqueous solutions may be capable of existence in these media.

It is significant that the chemical guideposts established in aqueous solutions at room temperature hold true to a good approximation in fused salt solutions even in the neighborhood of 1000°C.

The absorption spectra of the actinides in fused salts bear a striking resemblance to the aqueous solution spectra of the same oxidation state. This fact establishes a kind of correspondence principle which allows one to carry over deductions about chemical behavior based on spectral studies in aqueous solution to fused salt systems. Of particular interest are spectral changes having their origin in the formation of complex ions of one sort or another.

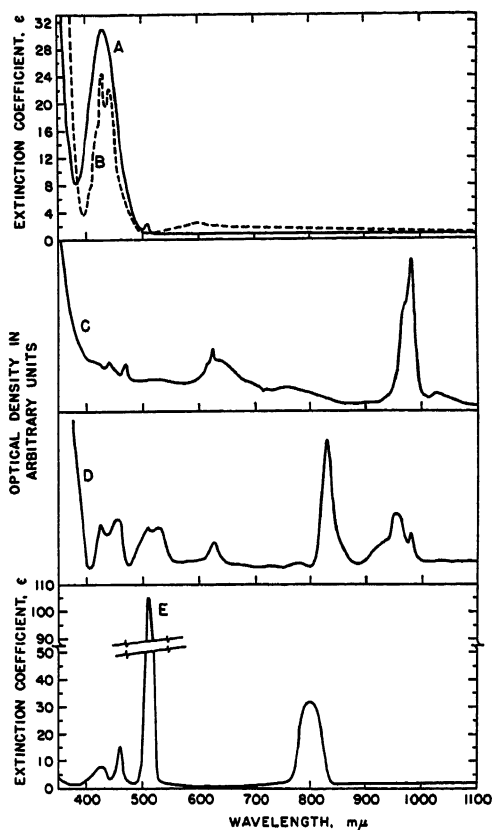


FIG. 4. Absorption spectra of actinide ions in fused nitrates.

Curve A: U(VI) in $\text{LiNO}_3\text{-KNO}_3$ eutectic at 160°C

Curve B: $\text{UO}_2(\text{II})$ in $\text{NH}_4\text{NO}_3\text{-LiNO}_3\text{-NH}_4\text{Cl}$ at 153°C

Curve C: Np(V) in $\text{LiNO}_3\text{-KNO}_3$ eutectic at 160°C

Curve D: Pu(VI) in $\text{LiNO}_3\text{-KNO}_3$ eutectic at 160°C

Curve E: Am(III) in $\text{LiNO}_3\text{-KNO}_3$ eutectic at 170°C

Complex Ions in Fused Salts

Complex ions in fused salts have in the past been studied primarily by electrochemical and cryoscopic means. The recent introduction of the spectrophotometric method can shed new light on these phenomena which are of vital importance to the chemistry of fused salt solutions.^{1, 2}

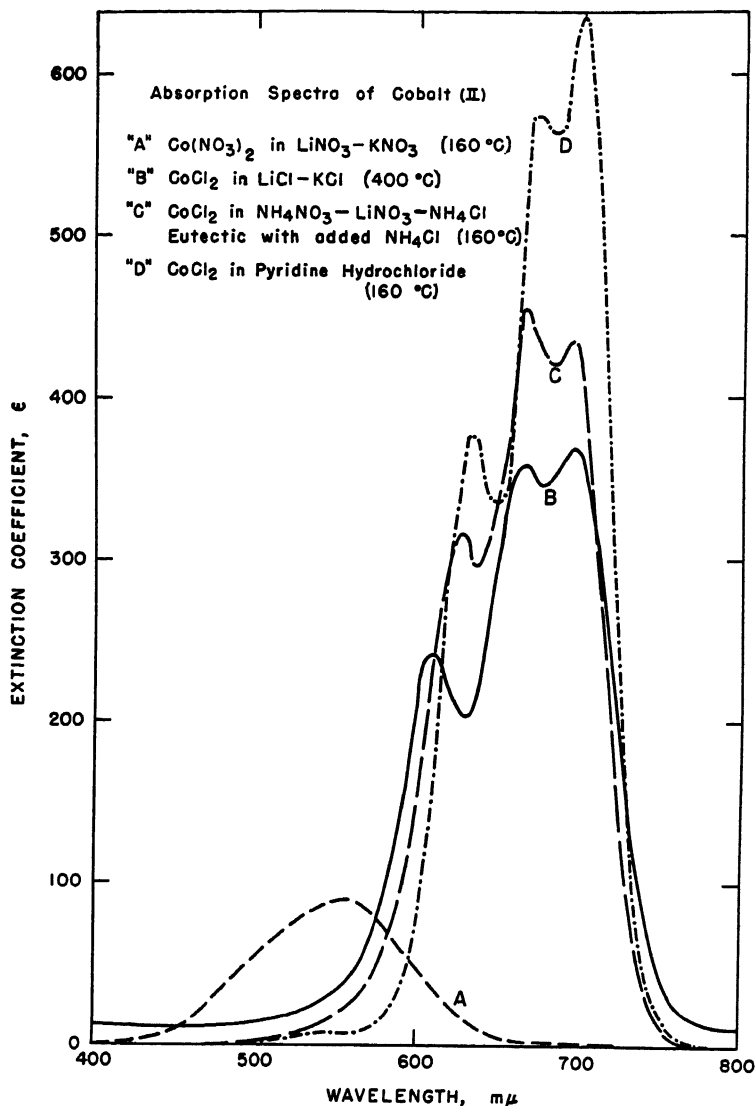


Fig. 5. Absorption spectra of Co(II) in different fused salts.

Complex Ions in Pure Chloride Melts.

Phase diagrams of numerous binary salt systems show that complex compounds frequently exist in the solid state and crystallographic studies on a number of these compounds have given detailed information on the spatial arrangement of the complex molecular groupings occurring within them.

Results have been published on the compounds Cs_2MCl_4 where $M = \text{Zn}, \text{Co}, \text{Ni}$ or

Cu and Cs_2MCl_6 where $M = \text{Th}, \text{U}, \text{Np}, \text{Pu}$.

Crystallographic studies on the Cs_2MCl_4 compounds have revealed that the metal atom M is surrounded tetrahedrally by four chloride ions.¹⁹⁻²¹ Crystallographic studies on the Cs_2MCl_6 compounds on the other hand have shown that the metal atom M is surrounded octahedrally by six chloride ions.^{9, 10}

The existence of the molecular groupings

MCl_4^- and MCl_6^- respectively in these two series of solid compounds appears to be very well established indeed. The existence of such molecular groupings in fused salts is however much less well established.

It has long been known that the absorption spectra of divalent Co, Ni, and Cu ions are different depending on whether the ions are octahedrally or tetrahedrally coordinated. The most spectacular example of this behavior is the divalent cobalt ion which is red in octahedral and blue in tetrahedral coordination.

By studying the absorption spectra of the solid compounds Cs_2MCl_4 and comparing them with the spectra of solutions of these compounds in pure chloride melts it has been possible to identify the tetrahedral complex ions CoCl_4^- , NiCl_4^- and CuCl_4^- in melts.

Crystals of the salt Cs_2ZnCl_4 were grown from aqueous solutions. Melts of this salt were found to be crystal clear and did not absorb light in the region 300–1200 $\text{m}\mu$.

Small amounts of the anhydrous metal chlorides CoCl_2 , NiCl_2 and CuCl_2 were dissolved in the melts and the absorption spectra measured. At the end of an experiment, the melt was allowed to solidify. A portion of the melt was ground to a fine powder, pressed into a transparent disc and the spectrum determined both at room temperature and at liquid nitrogen temperature. The very close similarity that was found in the spectra of the melts and the solids may be taken as strong evidence for the existence in melts of the tetrahedral chlorocomplexes of Co(II) ^{22, 23}, Ni(II) ^{24, 25} and Cu(II) . Similarly, evidence is found for MCl_6^- complex ions in fused salt solutions.

Complex Ions in Nitrate Melts. The spectrophotometric studies of solutions of the transition metal ions in chloride melts have clearly shown the existence of the fully complexed ions MCl_4^- and MCl_6^- . Very little can be learned about the stabilities of these complexes however from studies carried on

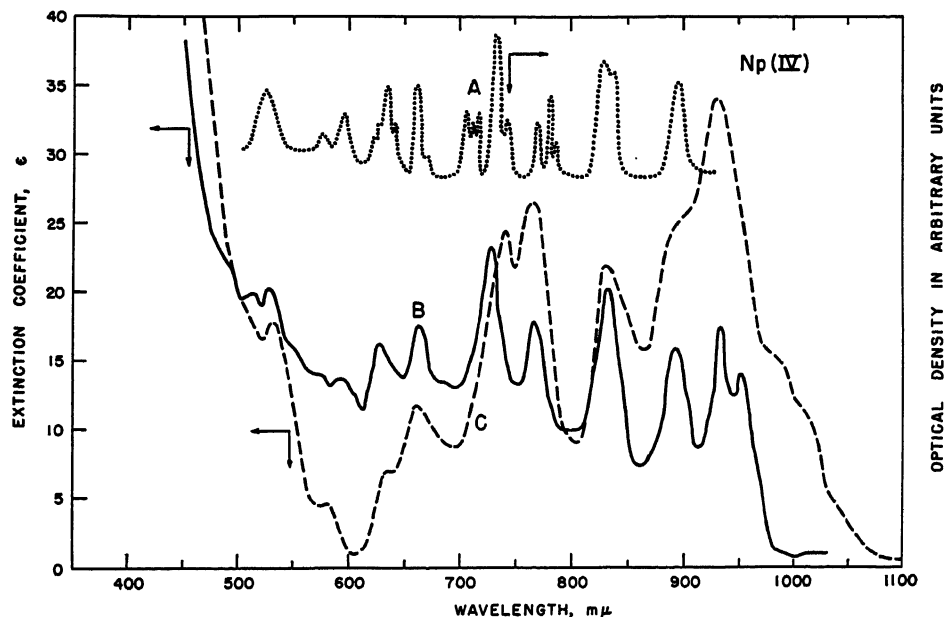


Fig. 6. Absorption spectra of neptunium.

Curve A: Cs NpCl_6 crystal at 80°K

Curve B: Np(IV) in pyridinehydrochloride at 160°C

Curve C: Np(IV) in LiCl-KCl eutectic at 400°C

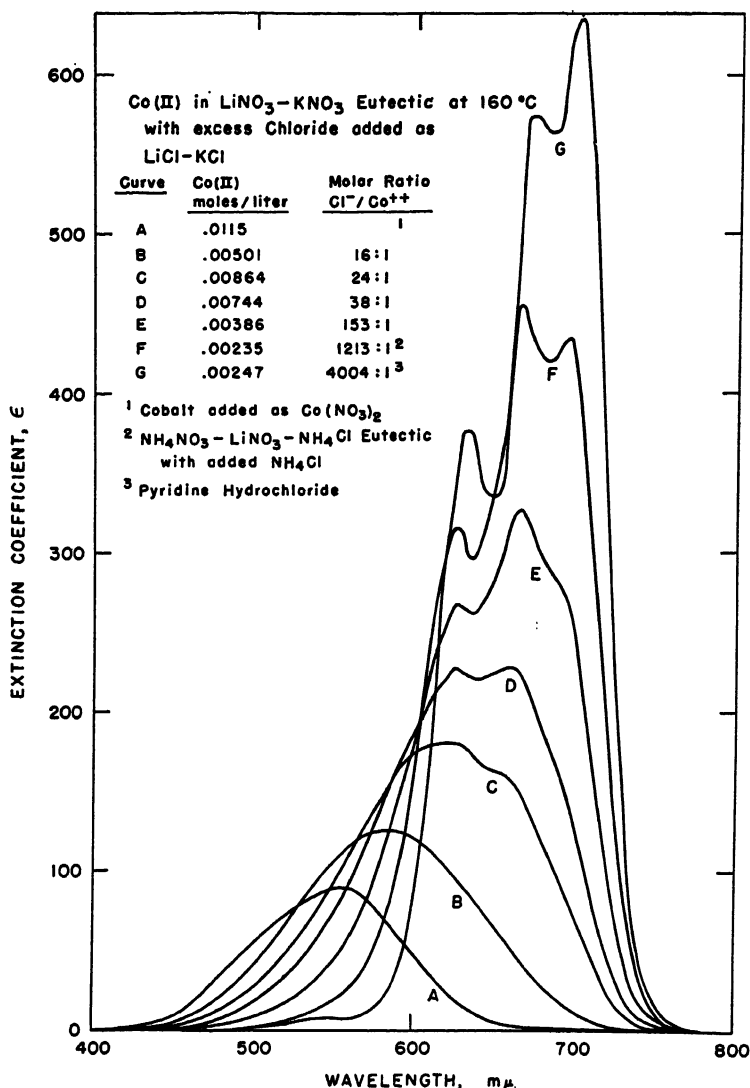


FIG. 7. Absorption spectra of Co(II) in LiNO₃-KNO₃ eutectic with varying chloride concentration at 160°C.

in pure chloride media. A solvent is required in which one can examine the equilibria involved in the formation of these complex ions. Such a solvent is the LiNO₃-KNO₃ eutectic.

The picture that evolves from these studies is that in the nitrate melt the divalent metal ions are surrounded by four nitrate groups tetrahedrally arranged in such a way that the twelve oxygens belonging to the four

nitrate groups are at positions equidistant from the central metal ion. The nitrate oxygens can, according to this model give rise to an electric field of cubic symmetry. In a similar way, the oxygen atoms of the six water molecules situated octahedrally about the divalent metal ions in aqueous solutions also give rise to an electric field of cubic symmetry. Thus it would appear that in fused nitrate media the oxygen coordination

to the central metal ions is in important ways similar to that found in aqueous solutions. The fused nitrate solutions then provide a medium in which to study complexing in much the same way as one studies complexing in aqueous solution.

Other recently reported work on ultraviolet absorption spectra includes the oxyanions nitrate, chromate and nitrite in a variety of fused-salt mixtures^(28a); and Co(II), Ni(II), Cr(III), in fused KSCN, and Sc(III), Ti(IV), V(III), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), in LiCl-KCl eutectic.^{28b}

In developing a solution chemistry in fused salts, some new approaches for the separation of metal ions from these media have been explored with some success. These include:

Chromatographic adsorption on Merck's γ - Al_2O_3 of transition metal cations dissolved in fused nitrates;²⁹ solvent extraction; formation of graphite lamellar^{30, 31} compounds; precipitations; volatilization, etc.

Metal Production. Fused alkali and alkaline earth halides are attractive media in which to carry out chemical reactions primarily because they span a large range of oxidation-reduction potentials. For example, the region of stability in LiCl-KCl eutectic is about 3.5 V and in CsCl-MgCl₂ eutectic is about 2.6 V at 700°C.³² By comparison, the region of stability of oxidizing and reducing agents in aqueous solutions at room temperature is approximately 1.2 V exclusive of overvoltages.³³

Of particular interest is the fact that many metals which react with water can be deposited successfully from fused salts.

In laboratory experiments, the metals Zr, Th, U and Np have been prepared from solutions in LiCl-KCl eutectic of ZrCl₄, ThCl₄, UCl₄ and NpCl₄ by reaction with Mg metal.

Uranium metal has also been prepared by reaction of the double salt Cs₂UCl₆ with Mg metal in a 50 mole % CsCl-50 mole % MgCl₂

fused salt matrix (m.p. 550°C). The salt Cs₂UCl₆ was chosen because it crystallizes in an anhydrous condition from aqueous solutions of tetravalent uranium and can be handled without special precautions.²⁶

REFERENCES

1. GRUEN, D. M., "Chromatography and Spectrophotometry of Fused Salts," *Nature*, **178**, 1181-2 (1956).
2. GRUEN, D. M., "Preliminary Spectrophotometric Study of Complex Ions in Fused Salts," *J. Inorg. Nucl. Chem.*, **4**, 74-76, (1957).
3. GRUEN, D. M., GRAF, P. AND FRIED, S., "Spectrophotometric and Chromatographic Studies of Actinide Ions in Fused Salts," Proceedings of the XVth International Congress of Pure and Applied Chemistry, Paris, July, (1957).
- 3a. GRUEN, D. M., AND MCBETH, R. L., "Oxidation States and Complex Ions of Uranium in Fused Chlorides and Nitrates," *J. Inorg. Nucl. Chem.* **9**, 290-301 (1959).
4. SUNDHEIM, B. R. AND GREENBERG, J., "High Temperature Modification of the Beckman DU Spectrophotometer," *Rev. Sci. Instr.*, **27**, 703-4 (1956).
5. LAITINEN, H. A., FERGUSON, W. S. AND OSTERYOUNG, R. A., "Preparation of Pure Fused LiCl-KCl Eutectic Solvent," *J. Electrochem. Soc.*, **104**, 516-520 (1957).
6. BURKHARD, W. J. AND CORBETT, J. D., "The Solubility of Water in Molten Mixtures of LiCl-KCl," *J. Am. Chem. Soc.*, **79**, 6361-3 (1957).
7. DIEKE, G. H. AND DUNCAN, A. B. F., "Spectroscopic Properties of Uranium Compounds," McGraw-Hill Book Co., Inc., New York, 1949.
8. GRUEN, D. M. AND FRED, M., unpublished work.
9. ZACHARIASEN, W. H., "Crystal Chemical Studies of the 5f-Series of Elements. II. The Crystal Structure of Cs₂PuCl₆," *Acta Cryst.*, **1**, 268-9 (1948).
10. SIEGEL, S., "The Structures of Cs₂ThCl₆ and Cs₂UCl₆," *Acta Cryst.*, **9**, 827 (1956).
11. STARITZKY, E. AND SINGER, J., "Optical and X-ray Data on a Group of Isostructural Uranium and Plutonium Compounds," *Acta Cryst.*, **5**, 536-40 (1952).
12. KRAUS, K. A. AND NELSON, F., "Hydrolytic Behavior of Metal Ions. I. The Acid Constants of Uranium(IV) and Plutonium(IV)," *J. Am. Chem. Soc.*, **72**, 3901-6 (1950).

ABSORPTION SPECTROMETRY—VISIBLE AND ULTRAVIOLET

13. STEWART, D. C., "Absorption Spectra of Lanthanide and Actinide Rare Earths," *ANL-4812*, (1952).
14. WU, T. Y. AND GOUDSMIT, S., "Low States of the Heaviest Elements," *Phys. Rev.*, **43**, 496 (1933).
15. SJOBLUM, R. AND HINDMAN, J. C., "Spectrophotometry of Neptunium in Perchloric Acid Solutions," *J. Am. Chem. Soc.*, **73**, 1744-51 (1951).
- 15a. GRUEN, D. M., MCBETH, R. L., KOOI, J. AND CARROLL, W. T., "Oxidation States of the Elements and their Potentials in Fused-Salt Solutions: The Actinide Elements," *Ann. N. Y. Acad. Sci.* **79**, 941 (1959).
16. AERLAND, S., "On the Complex Chemistry of the Uranyl Ion. I," *Acta Chem. Scand.*, **3**, 374-400 (1949).
17. CONNICK, R. E., KASHA, M., MCVY, W. H. AND SHELLE, G. E., "Spectrophotometric Studies of Plutonium in Solution," *NNES*, Vol. 14B, Paper 4.20, McGraw-Hill Book Co., Inc., New York, 1949.
18. PENNEMAN, R. A. AND ASPREY, L. B., "A Review of Americium and Curium Chemistry," *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, United Nations, New York, **7**, 355-362 (1956).
19. BREHLER, B., "Über das Cs_2ZnCl_4 ," *Z. Krist.*, **109**, 68-72 (1957).
20. PORAI-KOCHITZ, M. A., *Travaux de l'institut de cristallographie. Livraison 10. Communication au III Congrès international de cristallographie, Moscou*, (1954).
21. HELMHOLTZ, L. AND KRUH, R. F., "Crystal Structure of Cesium Chlorocuprate, Cs_2CuCl_4 , and the Spectrum of the Chlorocuprate Ion," *J. Am. Chem. Soc.*, **74**, 1176-81 (1952).
22. KATZIN, L., "Absorption Spectrum of Cs_2CoCl_4 at Liquid Nitrogen Temperatures," *J. Am. Chem. Soc.*, **76**, 3089-90 (1954).
23. GRUEN, D. M., AND MCBETH, R. L., "Tetrahedral $NiCl_4^{2-}$ Ion in Crystals and in Fused Salts. Spectrophotometric Study of Chloro Complexes of Nickel(II) in Fused Salts," *J. Phys. Chem.*, **63**, 393 (1959).
- 23a. SMITH, G. P. AND BOSTON, C. R., "Absorption of Fused-Salt Solutions," *Ann. N. Y. Acad. Sci.*, **79**, 930 (1959).
- 23b. HARRINGTON, G. AND SUNDHEIM, B. R., "Absorption Spectra in Molten Salts," *Ann. N. Y. Acad. Sci.* **79**, 950 (1959).
24. BALLHAUSEN, C. J., "Studies of Absorption Spectra. III. The Spectra of Ni(II) Complexes," *Kgl. Danske Videnskab. Selskab. Mat-fys. Medd.*, **29**, No. 8, (1955).
25. HORNYAK, F. M., "Color Transitions in Fused Nickel (II)—Alkali Halide Systems," *J. Am. Chem. Soc.*, **79**, 5435-37 (1957).
26. FERRARO, J. R., "Some Complex Chlorides of Uranium Tetrachloride and Thorium Tetrachloride," *J. Inorg. Nucl. Chem.*, **4**, 283-6 (1956).
27. VAN ARTSDALEN, E. R., "Complex Ions in Molten Salts. Ionic Association and Complex Ion Effect," *J. Phys. Chem.*, **60**, 172-77 (1956).
28. THOMPSON, S. G., HARVEY, B. G., CHOPPIN, G. R. AND SEABORG, G. T., "Chemical Properties of Elements 99 and 100," *J. Am. Chem. Soc.*, **76**, 6229-31 (1954).
29. KRAUS, K. A. AND NELSON, F., "Symposium on Ion Exchange and Chromatography," *Am. Soc. Mat. Testing*, Atlantic City, June (1956).
30. CROFT, R. C., "New Molecular Compounds of the Layer Lattice Type," *Australian J. Chem.*, **9**, 184-93 (1956).
31. DZURUS, M. L. AND HENNIG, G. R., "Graphite Compounds," *J. Am. Chem. Soc.*, **79**, 1051-54 (1957).
32. DELIMARSKII, YU. K., "Electrode Potentials of Metals in Molten Salts," *J. Phys. Chem.*, (U.S.S.R.), **29**, 28-38 (1955).
33. LATIMER, W. M., "Oxidation Potentials," Second Edition, Prentice-Hall, Inc., New York, 1952.

G. L. CLARK

LONG PATH ULTRAVIOLET ABSORPTION SPECTROPHOTOMETRY

The spectral region of particular interest (2200-4000Å), which is associated with energy level transitions of outer electrons, has been used in chemical analysis for measuring the presence and concentration of gases and vapors in trace amounts [parts per million by vol. (ppm)].

The essential components of a spectrophotometer for long path studies beyond those necessary for conventional (short path) use are:

(1) A light source of high and constant intensity over the spectral region of interest. For this component one may choose from the following:

- (a) High pressure xenon arc.
- (b) Mercury H6 or H4 arcs.

- (c) Carbon arc.
- (d) Hydrogen arc.
- (e) The sun.

(2) A dispersing system which minimizes attenuation by the dispersing medium (quartz). Fresnel-type assembly of fused quartz elements is recommended when radiation intensities are marginal.

(3) A high sensitivity detector cell such as the 1P28 photomultiplier.

Astrophysicists have used the long path technique to measure the concentration of ozone in the atmosphere near the surface over long horizontal paths (1 to 2 miles) in the spectral region 2400 to 3100Å and obtained values from 0 to 0.03 ppm. Using the sun as the light source, ozone in the upper atmosphere has been detected and its concentration determined.

In extending the technique to such gases as sulfur dioxide, nitrogen dioxide, and vapors of organic compounds one should determine the analytical wavelength for the particular material only after one has compared ratios of attenuation at various wavelengths. This is particularly true when dealing with mixtures of gases and vapors in air. The normal atmosphere attenuates ultraviolet radiation rapidly in the spectral region 2200–2700 due to Rayleigh scattering and to a lesser degree by oxygen molecule absorption.

In principle, long paths may be achieved by folding of the light beam through the use of plane or spherical mirrors. Although this has worked well in the infrared, large reflection losses severely limit this technique in the ultraviolet.

N. A. RENZETTI

MANGANESE DETERMINATION

Spectrophotometric methods for the determination of manganese are uniquely characterized by the almost exclusive adaptation of the permanganate procedure. This method

is very sensitive and sufficiently selective that other procedures for determining manganese have not heretofore received serious consideration.

The formation of the permanganate ion by the oxidation of manganese(II) appears to have been first suggested by Crum¹ in 1845 while the first analytical method was given by Richard² in 1872. In acid medium, manganese(II) may be oxidized by lead dioxide, sodium bismuthate, sodium hypochlorite or sodium persulfate, but the oxidation with sodium periodate³ appears to be the best procedure for general applicability. The periodate oxidation proceeds smoothly and rapidly in hot sulfuric or nitric acid solution, and an excess of reagent does not interfere with the color development. The concentration of acid is not critical, but the rate of the reaction increases with increasing acid concentration, and concentrations greater than 3 *N* are recommended except for solutions containing very small amounts of manganese where a 2 *N* acid solution provides the most rapid oxidation. Standard permanganate solutions prepared using the periodate oxidation are remarkably stable and have been stored for 7 months without a measurable change in the color absorption.⁴

The permanganate ion strongly absorbs light between 480 and 580 *mμ*. Well-defined absorption maxima are observed at 526 and 546 *mμ* with shoulders at 566, 508, and 490 *mμ*.⁵ The molar absorbance index of the permanganate ion is about 2300 near 526 *mμ*.⁶ Beer's law is obeyed for solutions containing less than 150 ppm manganese. The usual working range of concentrations is approximately 0.2 to 20 ppm, but the determination of 0.01 ppm manganese has been reported in sea water.⁷

A comprehensive study of interferences⁸ reveals that colored species and all reducing agents may interfere and must be compensated or separated prior to the oxidation. Organic matter should be destroyed by fuming with nitric acid or a mixture of nitric

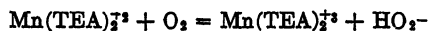
and sulfuric acids. Colored ions such as cerium(IV), cobalt(II) and nickel(II) must be compensated or separated, although small concentrations of copper(II) and chromium(II) do not interfere seriously. Chromium(III) is slowly oxidized by periodate, and the resulting dichromate interferes at wavelengths shorter than about 565 m μ . Permanganate may, however, be determined at 575 m μ in the presence of large concentrations of dichromate. The ubiquitous iron(III) is best removed by complexing with *o*-phosphoric acid, which also helps to prevent the precipitation of the slightly soluble iron(III) and manganese(III) periodates. In order to compensate for many colored species, a bleached blank may be prepared by adding one or two drops of a very dilute solution of hydrogen peroxide to the permanganate solution after measurement.⁶ In most cases, the hydrogen peroxide will react only with the permanganate, and the small excess of peroxide will not affect the color of other species. If interferences are observed, sodium nitrite solution or sodium azide may be used in place of the hydrogen peroxide.

Traces of chloride and iodide are oxidized by periodate, but appreciable quantities of halides should be removed by fuming the sample with sulfuric acid prior to the oxidation. If the concentration of chloride is extremely large, the manganese(II) can be extracted into chloroform with 8-hydroxyquinoline, the oxine destroyed with hydrogen peroxide and perchloric acid, and the manganese(II) then oxidized with periodate.

The principal limitation of the periodate procedure is the rate of oxidation which, for very dilute manganese solutions, may be so slow as to preclude quantitative oxidation within two to three hours, even when using silver(I) as a catalyst.⁹ While the persulfate oxidation has for years been considered inferior to the periodate procedure, a careful re-examination of the persulfate method indicates that it probably is advantageous for the very dilute manganese solutions.¹⁰ The

persulfate oxidation of manganese is more rapid than that using periodate. Furthermore, organic matter is oxidized sufficiently rapidly by the persulfate and permanganate that prior oxidation of small amounts of organic matter is not required. Halide ions need not be separated but may be complexed with mercury(II) to prevent reduction of the permanganate. The minimum concentration of silver(I) required to catalyze the manganese oxidation is considerably smaller than that previously thought necessary and varies from 10⁻⁶ to 10⁻⁸ *M* depending upon the nature of the acid solution.

A recent method for the spectrophotometric determination of manganese utilizes the green manganese(III)-triethanolamine complex.¹¹ In alkaline triethanolamine solutions, the manganese(II)-triethanolamine complex is air oxidized according to the reaction



The manganese(III) complex exhibits a broad absorption maximum at 438 m μ , the molar absorbance index of which is 200. Although much less sensitive than the permanganate procedure, the simplicity and selectivity of this method offer considerable promise, particularly to the mineral and agricultural industries. The oxidation reaction is complicated by the fact that manganese(III) may react with hydroperoxide produced by the reduction of the oxygen to form a red complex which interferes with the determination. However, the hydroperoxide complex is easily decomposed by performing the oxidation in a hot solution containing bromate. Only oxygen and lead tetroxide, Pb₃O₄, will effect the oxidation. For this reason, a more suitable procedure for effecting the oxidation utilizes the addition of a few milligrams of lead tetroxide. The lead tetroxide decomposes the hydroperoxide, and the excess reagent dissolves to form the lead(II)-triethanolamine complex which does not interfere with the manganese determina-

tion. Beer's law is obeyed for solutions containing less than about 350 ppm manganese. A convenient working range is 30 to 250 ppm, but because of the small absorbance index, the permanganate method is preferred for solutions containing less than about 25 ppm.

Most metal ions do not interfere with the manganese determination. Silver(I) and titanium(III) give precipitates in alkaline solution which may be removed by filtration. The blue copper(II)-triethanolamine complex is transparent at 438 m μ , but large concentrations of cobalt(II) and nickel(II) are not permissible. Chromium(III) interferes more seriously and must be compensated or separated.

Other methods for determining manganese have received only scattered attention. No methods based on the ultraviolet absorption of manganese complexes have received serious consideration although in principle such procedures are feasible, particularly under circumstances where the numerous interfering metal ions are not likely to be present. A number of organic compounds have been used to form colored products with the higher oxidation states (III, IV, VII) of manganese. Among these may be mentioned benzidine,^{4, 12, 13} diethyldithiocarbamate,^{14, 15} formaldoxime,¹⁶⁻¹⁹ o-tolidine,²⁰ p-dimethylaminoaniline,^{21, 22} 4,4'-tetramethyldiaminodiphenylmethane,²³⁻²⁶ 4,4'-tetramethyldiaminotriphenylmethane,²⁷⁻²⁹ as well as pyrophosphoric acid³⁰ and alkaline tellurate.³¹ In general, these methods are unspecific, and many metal ions may be expected to interfere in each procedure. Often the colors produced are very intense though not appreciably stable. Using the benzidine procedure, for instance, concentrations of the order of 8 parts per billion are readily determined, but the color fades rapidly and is not stable for more than a few minutes. Tetramethyldiaminotriphenylamine, with a sensitivity of about 1 part per billion, provides the most sensitive method known for determin-

ing manganese. Recent investigations indicate the color formed by this reagent may be sufficiently stable to provide a feasible method for determining traces of manganese,^{28, 29} but the color is a function of the acid medium, and further study of this reagent is warranted. It may be noted that most of the above methods utilize the ability of the organic nitrogen to coordinate with the manganese to stabilize a higher oxidation state.

Applications and detailed procedures for the various methods may be found in the excellent treatises by Sandell³² and Snell and Snell.³³

REFERENCES

1. CRUM, W., 55, 219 (1845).
2. RICHARD, P., *Compt. rend.*, **75**, 1821 (1872).
3. WILLARD, H. H. AND GREATHOUSE, L. H., *J. Am. Chem. Soc.*, **39**, 2366 (1917).
4. CLARK, N. A., *Ind. Eng. Chem. (Anal. Ed.)*, **5**, 241 (1933).
5. LANGE, B. AND SCHUSTERIUS, C., *Z. physik. Chem.*, **A159**, 295 (1932).
6. ROWLAND, JR., G. P., *Ind. Eng. Chem. (Anal. Ed.)*, **11**, 442 (1939).
7. THOMPSON, T. G. AND WILSON, T. L., *J. Am. Chem. Soc.*, **57**, 233 (1935).
8. MEHLIG, J. P., *Ind. Eng. Chem., (Anal. Ed.)*, **11**, 274 (1939).
9. KOROLEFF, F., *Acta Chem. Scand.*, **1**, 503 (1947).
10. NYDAHL, F., *Anal. Chim. Acta*, **3**, 144 (1949).
11. NIGHTINGALE, JR., E. R., *Anal. Chem.*, **31**, 146, 958 (1959).
12. STRATTON, R. C., FICKLEN, J. B., AND HOUGH, W. A., *Ind. Eng. Chem. (Anal. Ed.)*, **4**, 2 (1932).
13. WIESE, A. C. AND JOHNSON, B. C., *J. Biol. Chem.*, **127**, 203 (1939).
14. SPECKER, H., HARTCAMP, H. AND KUCHTNER, M., *Z. anal. Chem.*, **143**, 425 (1954).
15. WYATT, G. F., *Analyst*, **78**, 656 (1953).
16. GOTTLIEB, A. AND HECHT, F., *Mikrochemie ver Mikrochem. Acta*, **35**, 337 (1950).
17. KNIPPHORST, L. C. E., *Chem. Weekblad*, **42**, 328 (1946).
18. SIDERIS, C. P., *Ind. Eng. Chem. (Anal. Ed.)*, **9**, 445 (1937); **12**, 307 (1940).
19. WAGENAAR, G. H., *Pharm. Weekblad*, **75**, 641 (1938).

20. FORMAN, L., *J. Am. Water Works Assoc.*, **21**, 1212 (1929).
21. SCHMIDT, R., *Chem.-Ztg.*, **51**, 1015 (1927).
22. WENGER, P., DUCKERT, R. AND BUSSET, M. L., *Helv. Chim. Acta*, **24**, 1143 (1941).
23. CORNFIELD, A. H. AND POLLARD, A. G., *J. Sci. Food Agr.*, **1**, 107 (1950).
24. HARRY, R. G., *Chem. and Ind.*, **50**, 796 (1931); *J. Soc. Chem. Ind.*, **50**, 434T (1931).
25. NICHOLAS, D. J. D. AND FISHER, D. J., *Ann. Rept. Agr. and Hort. Research Sta., Long Ashton, Bristol*, 1950, 115.
26. PRODINGER, W. D., *Mikrochemie ver Mikrochem. Acta*, **36/37**, 580 (1951).
27. GATES, E. M., AND ELLIS, G. H., *J. Biol. Chem.*, **168**, 537 (1947).
28. SCHWARZ, G., FISCHER, O. AND HAGEMAN, B., *Deut. Molkeri-Ztg.*, **64**, 143 (1943).
29. YUEN, S. H., *Analyst*, **83**, 350 (1958).
30. TOMULA, E. S. AND AHO, V., *Ann. Acad. Sci. Fennicae*, **A52**, No. 4 (1939); **A55**, No. 1 (1940).
31. TOURKY, A. R., ISSA, I. M. AND HEWAIDY, J. F., *Anal. Chim. Acta*, **16**, 151 (1957).
32. SANDELL, E. B., "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., 3rd ed., New York, 1959.
33. SNELL, F. D. AND SNELL, C. T., "Colorimetric Methods of Analysis," D. Van Nostrand, Inc., 3rd ed., New York, 1949, vol. II.

E. R. NIGHTINGALE, JR.

MICROSPECTROPHOTOMETER OF SIMPLIFIED DESIGN

The use of sensitive high-speed spectrophotometry for the investigation of the pigment system within living plant and animal cells has only begun to be investigated. Recent progress in this research has been summarized in several reviews.^{1, 2} The methods of precision spectrophotometry still require fairly complicated apparatus, and all employ a photomultiplier tube as the light-sensitive photocell.

A microspectrophotometer using solid-state electronic components has been constructed in our laboratory and is being used to investigate pigmented structures in living cells. The light-sensitive element is a cadmium selenide photoconductive cell. The

photocell output is amplified by a transistorized d-c amplifier and displayed on an oscilloscope used as a d-c voltmeter. For some time, photoconductive cells have been used for spectral measurements in the infrared region. More recently they have been used for x-ray spectroscopy.³ However, the present application of these cells to visible and ultraviolet microspectrophotometry is novel.

In Fig. 1 are shown a diagram of the instrumental setup and a photograph of the assembled apparatus in use. Light from source L enters a grating monochromator G, as shown by the dotted line. The exit slit of the monochromator is focused by a quartz lens on the condenser of microscope M. After passing through the specimen, the light beam hits the photosensitive cell C, which is accurately positioned relative to the image and located 25 centimeters above the eyepiece of the microscope. The electrical signal from the photocell is amplified by the d-c amplifier A and displayed on a Dumont Model 403 oscilloscope D. The oscilloscope is used here because of its high d-c amplification capabilities; a high-impedance voltmeter would be just as satisfactory.

The microspectrophotometer uses either a xenon arc or a tungsten ribbon filament light source, a Bausch & Lomb 250-mm grating monochromator, and reflecting microscope optics (50 X, with numerical aperture of 0.5) purchased from the American Optical Co. With these components, the instrument is usable over the wavelength range from 200 to 990 m μ (millimicrons) in a single sweep for specimen areas of 16 μ^2 . For specimen areas of the order of 2 μ^2 , the useful range is 270 to 990 m μ . With a tungsten ribbon light source, the useful range is 370 to 900 m μ .

The actual construction of the instrument was greatly facilitated by taking advantage of a photomicroscopy setup, as shown in Fig. 1. The lower end of a rubber, light-tight bellows fits over the eyepiece of the micro-

MICROSPECTROPHOTOMETER OF SIMPLIFIED DESIGN

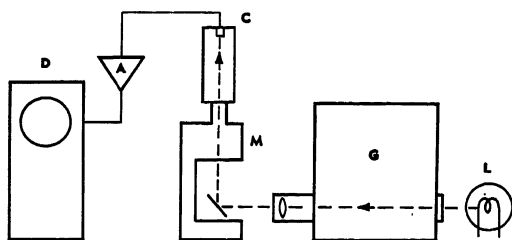
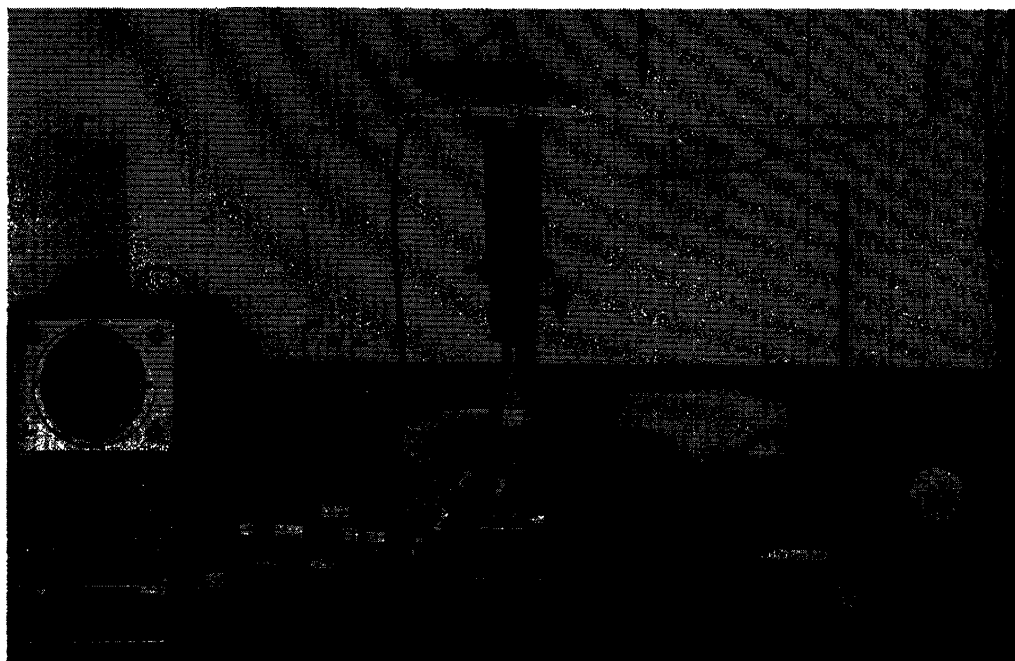


FIG. 1. Microspectrophotometer showing light source (L), monochromator (G), microscope (M), photoconductive cell (C), d-c amplifier (A), and oscilloscope (D). The microspectrophotometer in use. (photograph)



scope. The upper end of the bellows fits into a light-tight tube. At the other end of the tube may be placed either the ground-glass viewer or the photocell holder, by operating a sliding track. The entire upper assembly is swung into place by means of a vertical bar arrangement mounted on a base plate. The height of the photocell can be adjusted by telescoping the tube supporting it.

The photoconductive cells being used at present are general-purpose cells made by the Clairex Corp. of New York. Two sizes are available with sensitive areas of 0.5 by 1 and 1.6 by 4.7 millimeters. For a magnification of 500, these sizes represent specimen areas of about 2 and 30 μ^2 , respectively. The

spectral response of the cadmium selenide cells extends all the way from the far ultra-violet to the near infrared, with a rather sharp cutoff at about 1 μ . The peak response is in the visible region of the spectrum. At high light intensity, the time constant of the cell is of the order of milliseconds. At low light levels, the time constant is of the order of seconds. The sensitivity of the photocells per unit area is comparable to photomultiplier tube performance. In common with most photosensitive devices,⁴ these photocells show fatigue. After a period of use, the sensitivity decreases and the photocell must be replaced.

In practice, the photocell acts as a light-

sensitive resistor. In the dark, its resistance is greater than 100 megohms. In strong light its resistance decreases to the order of 1 megohm or less. The photocell used here is connected in series with a bias battery (70 to 100 volts) and a load resistor of 1 megohm. The load resistor serves as the input to the photocell amplifier, which is chopper-stabilized and battery-powered. The circuit employs two transistors in the common emitter configuration. Further d-c amplification is furnished by the oscilloscope used for output readings.

With the exception of arrangements similar to the one used by Denton,⁶ microspectrophotometers are generally rather elaborate instruments.^{1, 6, 7} They employ either split- or dual-beam optical systems with mechanical beam-chopping devices, voltage-regulated photomultiplier tubes with feedback mechanisms, and automatic-recording outputs. The final result of this type of instrumentation is a quantitative measurement of the optical density of a given specimen with an instrumental error of less than 5 per cent. Measurements from the ultraviolet through the visible range are recorded in a few minutes, and response times of the instruments are usually of the order of a few milliseconds. In order to record spectra from samples of very small area, relatively high magnification is usually necessary.⁶ At present, the microspectrophotometer described here is not to be compared with these. This instrument is portable in the sense that it can be assembled and used in the field. The maximum magnification employed to date is 500. At this magnification, spectra from areas of $2 \mu^2$ are easily obtained. Optical alignment is not critical, and the effects of stray light have been found to be negligible. No optical chopping is used, mainly because of the relatively long time constant of the photocell. Since the entire photosurface of the cell is exposed to the light beam, no effects due to variation in the sensitivity of the photosurface are observed.

A simple resistance-capacitance filter is employed at the amplifier output, resulting in an instrumental time constant of 2 seconds.

The photocell output as a function of the intensity of the incident light was investigated by comparison with the output of an RCA 926 phototube calibrated in our laboratory. Linearity of photocell output within 2 per cent with incident light intensity was observed except for very low light levels, which are not normally encountered with this instrument.

Although the present instrument uses the d-c output of the photocell for signal voltage, this is not meant to imply that direct amplification is the optimum in electronic design for this instrument. Experiments with the Clairex photocells used here indicate that chopping the incoming light beam at about 40 cycles per second, with subsequent a-c amplification and rectification will also produce a usable signal level.

At present, the instrumental noise level is determined by the light source and the amplifier fluctuations rather than by the noise in the photocell. For the Soret band peak of a single human blood cell, the oscilloscope noise level was 2.5×10^{-3} optical density units at a wavelength setting of 420 m μ and an entering band-width of 2 m μ . Although the useful optical density range of the instrument depends upon the wavelength setting and the intensity of the incident light, data taken to date indicate an upper limit of 1.5 optical density units before serious inaccuracies occur.

The procedure for obtaining an absorption spectrum with the apparatus in its present form is relatively simple. The area of interest in the specimen is located on a marked ground-glass screen at the top of the apparatus. The photocell is then put in position, and the dark current is balanced out with bias voltage. At each desired wavelength setting, one reading is taken over the specimen and another over a reference area by moving the cell assembly from one area to

the other. Before another reading is taken, the dark current level is checked and set to zero. The time required to determine a spectral curve depends upon the number of wavelength settings desired and the time constant of the photocell. For a 10 $m\mu$ interval over the range from 400 to 700 $m\mu$, the time required is about 20 minutes.

Because of the simplicity of the microspectrophotometer design, the demands made upon the operator are greater than those made by an automatically controlled instrument. For each specimen under investigation one must choose optimum values for the monochromator slit widths, which govern both the purity and the intensity of the light entering the system. In addition, one has a choice between critical or Köhler (even) illumination of the specimen. For critical illumination the image of the exit slit of the monochromator appears in the ob-

ject plane, and the light intensity is greater than it is when the specimen is evenly illuminated. Both of the foregoing factors depend upon the choice of magnifying power.

Applications. This instrument was designed primarily to make relatively short *in situ* spectral analyses on pigment granules and photoreceptor structures—that is, chloroplasts, chromatophores, and the retinal rods and cones of the eye. Use of these structures, which in general contain pigments in relatively high concentration, reduces the sensitivity requirements of the instrument. In addition to determining spectral absorption, the instrument is ideally suited for scanning single cells' or small organisms at fixed wavelengths in order to geometrically locate cell constituents which have characteristic absorption peaks.

The complete spectral range of the instrument is illustrated graphically in Fig. 2,

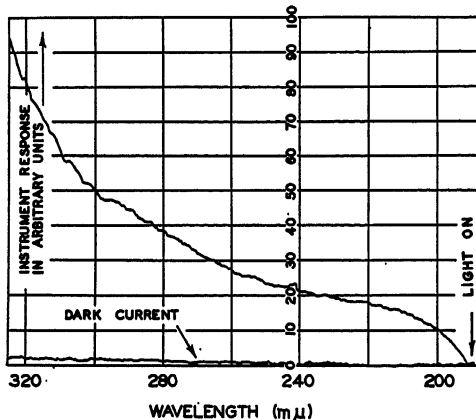
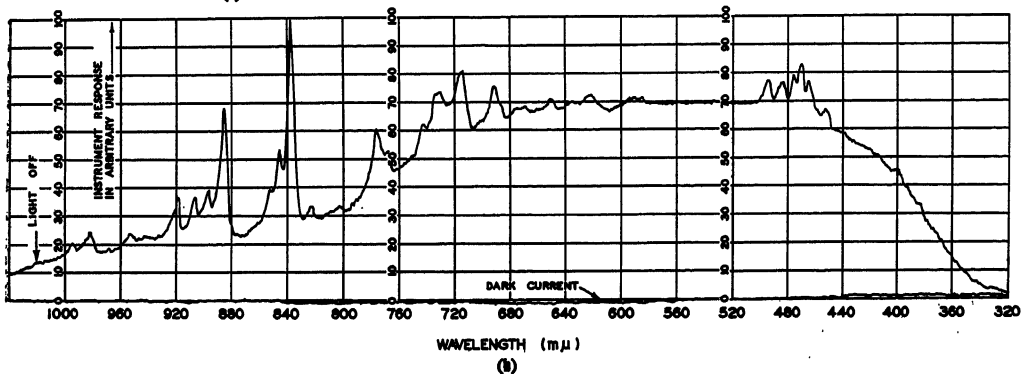


FIG. 2. Microspectrophotometer response as a function of the wavelength of the incident light (a) from 200 to 320 $m\mu$ and (b) from 320 to 1000 $m\mu$, with reduced intensity of incident light.



ABSORPTION SPECTROMETRY—VISIBLE AND ULTRAVIOLET

which shows the recorded output of the photocell over the range 200 to 1000 $m\mu$. The recordings were obtained with a Varian G-10 recorder connected to the amplified photocell output, set for 50 millivolts full scale. The wavelength drum of the monochromator was turned by hand throughout the spectral ranges indicated. In Fig. 2a, the entrance half-bandwidth was 2.6 $m\mu$ and the incident light was used at full intensity. In Fig. 2b, the half-bandwidth was 2 $m\mu$, and the intensity of the incident light was greatly reduced to keep the recorder pen on scale at the peaks. For wavelengths greater than 600 $m\mu$, the second-order grating spectrum was filtered out. The series of response peaks around 460 $m\mu$ and in the region 800 to 1000 $m\mu$ is due to line spectra of the xenon arc light source. For both of the response curves the microscope was focused on a blank quartz slide at a magnification of 175, representing a specimen area of 16 μ^2 .

The performance of the microspectrophotometer has been checked with bandpass filters, line spectra, and materials with known absorption peaks. In Fig. 3 are

plotted response curves for Bausch & Lomb interference filters Nos. 33-78-36 and 33-78-43 and for a Baird Associates interference filter No. 7-3470-3; the major peaks of these filters are at 368, 436, and 560 $m\mu$, respectively. These absorption curves are in excellent agreement with those obtained with a Beckman model DK recording spectrophotometer for the same filters.

Absorption spectra (not shown) have been obtained from single human blood cells. These showed characteristic absorption peaks at 418, 538, and 578 $m\mu$. In Fig. 4 are illustrated two transverse scans across a single human blood cell with wavelength settings of 417 and 500 $m\mu$, respectively. The difference between the two curves is a rough indication of the hemoglobin distribution within the blood cell as a function of cell diameter. The specimen area under investigation was slightly less than 2 μ^2 , and the results are in good agreement with published data.^{8,9}

Figure 5 shows the absorption spectrum in the visible region of a single chloroplast within the algal flagellate *Euglena gracilis*

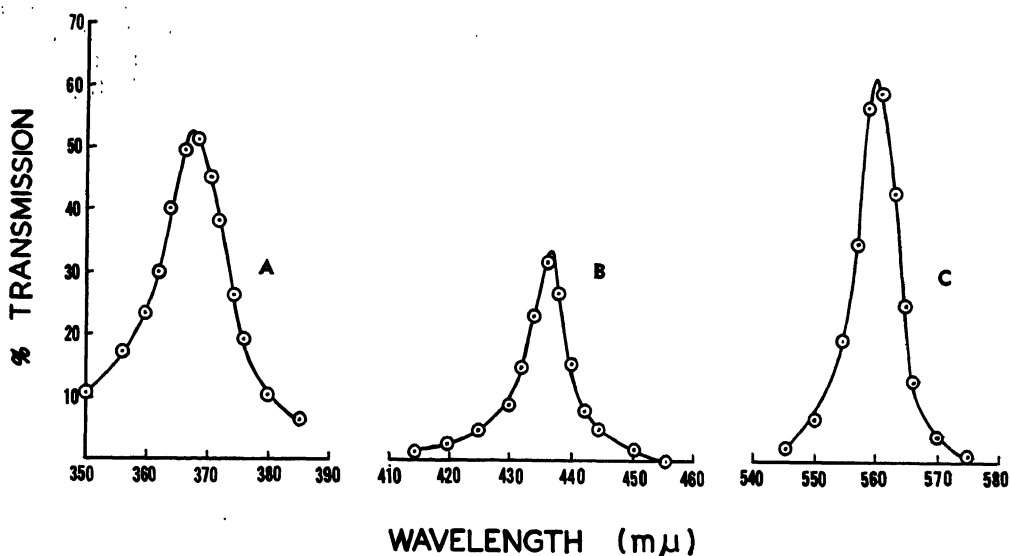


FIG. 3. Spectral response curves for three different interference filters with maxima at 368, 436, and 560 $m\mu$, respectively. Filter A is Bausch & Lomb No. 33-78-36; B is Bausch & Lomb No. 33-78-43; C is Baird Associates No. 7-3470-3. Incident half-bandwidth, 2 $m\mu$.

(open circles) compared with the spectrum of a chloroplast from *Chlorella* (solid circles) taken from the data of Swift and Rasch.¹ The average size of *Euglena gracilis* is 50 by 15 μ , and the green chloroplasts are on the order of 1 by 6 μ .¹⁰ The magnification was 250, representing a specimen area of 8 μ^2 . The reference area was the clear region in the cytoplasm adjacent to the chloroplast. The major absorption peaks at 415 to 430 $m\mu$ and at 680 $m\mu$ are in agreement with the data for chlorophyll A in living algae,¹¹ and the secondary peak at 480 $m\mu$ is due to the presence of carotenoids, which are known to be present in the chloroplasts.¹¹ The absorption spectrum shown in Fig. 5 is also in good agreement with the spectrum for cell suspensions of *Euglena* obtained in our laboratory.¹²

The microspectrophotometer has also been used¹³ to investigate the brightly colored oil globules found in the retina of birds, occurring mainly between the inner and outer segments of the cones.¹⁴ These colored globules are red, green, yellow, orange, and other, mixed, colors; they range from 3 to 5 μ in diameter, and their exact physiological role is not known.^{6, 13} Figure 6 shows absorption spectra for red, yellow, and green globules measured *in situ*. The vertical lines indicate the observed variability for each colored globule. These spectra were measured at a magnification of 500 through a specimen area of 2 μ^2 . The reference area was immediately adjacent to the globules and contained a slight amount of retinal material. Spectra taken of globules completely isolated from retinal material indicated no significant error resulting from this procedure over the wavelength range under investigation. These results indicate that the different colored globules within the retina can act as band pass color filters if they are suitably located in relation to a photosensitive pigment.^{6, 15} The spectral curves shown in Fig. 6 indicate the presence of carotenoids, a finding in agreement with the biochemical

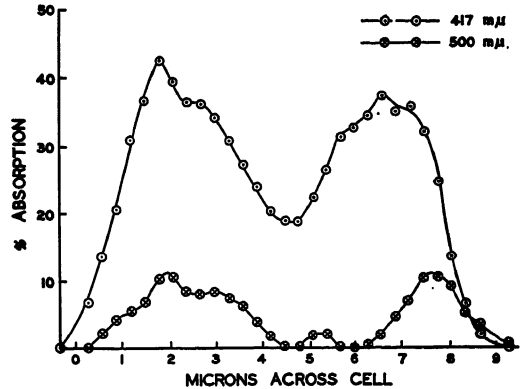


FIG. 4. Spectral absorption at fixed wavelengths of 417 and 500 $m\mu$ as a function of the distance across a single human blood cell.

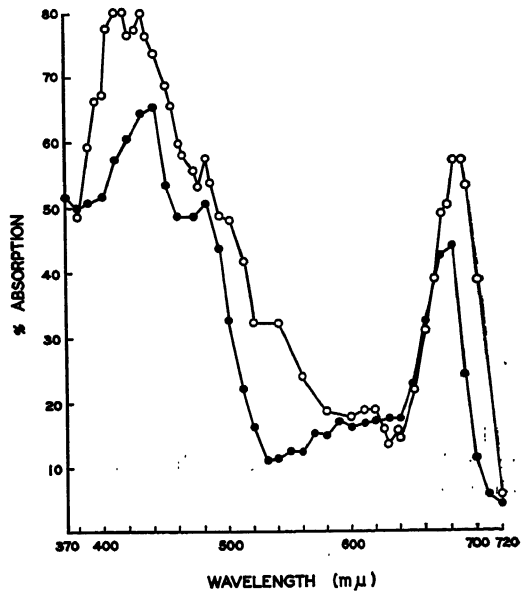


FIG. 5. Absorption spectrum of a single chloroplast of *Euglena gracilis* (open circles) compared with the spectrum of a single chloroplast of *Chlorella* (solid circles), taken from the data of Swift and Rasch.¹

investigation of Wald and Zussman¹⁵ on retinal extracts of chicken.

The illustrated spectra described are only an indication of the possible usefulness of the instrument. The microspectrophotometer is well suited for study of the effects of chemical and physical environment on the

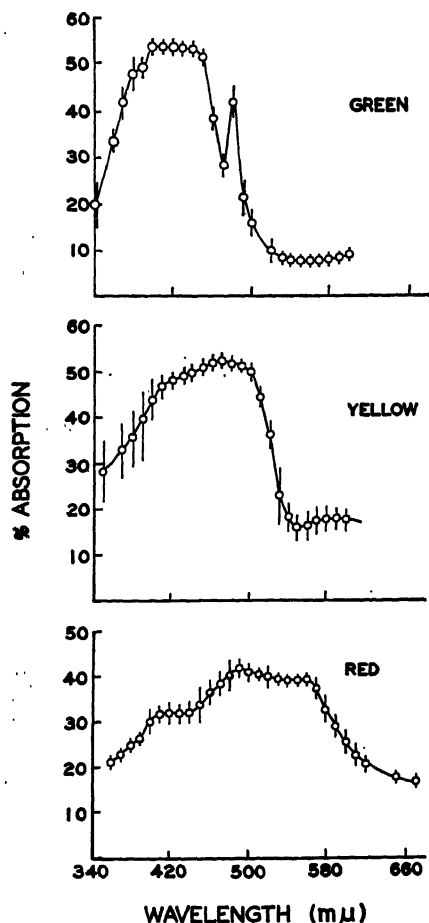


Fig. 6. Absorption spectra, measured *in situ* for red, yellow, and green globules within the chicken retina.

synthesis and concentration of pigments within a single cell or of organelles within a cell.¹⁷

REFERENCES

1. SWIFT, H. AND RASCH, E., in "Physical Techniques in Biological Research," G. Oster, and A. W. Pollister, Eds. (Academic Press, New York, 1956), vol. 3, p. 354; P. M. B. Walker, *ibid.*, p. 401.
2. LITVIN, F. F., *Biophysics*, 3, 1 (1958) (translated from the Russian by Pergamon Press); POLLISTER, A. W. AND ORNSTEIN, L., in "Analytical Cytology," R. C. Mellors, Ed. (McGraw-Hill, New York, 1955), chap. 1, p. 3; NORNBERGER, J. L., *ibid.*, chap. 4, p. 1; BLOUT, E. R., "Advances in Biol. and Med.

- Phys.," 3, 286 (1953); THORELL, B., *ibid.*, 6, 95 (1958).
3. HENRY, B. AND COLE, H., *Rev. Sci. Instr.* 30, 90 (1959).
4. DONALDSON, P. E. K., "Electronic Apparatus for Biological Research," Butterworths Scientific Publications, London, 1958.
5. DENTON, E. J. AND WALKER, M. A., *Proc. Roy. Soc. (London)*, B148, 257 (1958).
6. HANAOKA, T. AND FUJIMOTO, K., *Japan J. Physiol.*, 7, 276 (1957).
7. THORELL, B. AND AKERMAN, L., *Exptl. Cell Research, suppl.* 4, 83 (1957); CHANCE, B., *Rev. Sci. Instr.* 30, 735 (1959).
8. JOPE, E. M., in "Haemoglobin," Roughton, F. W. J. and Kendrew, J. C., Eds. (Interscience, New York, 1949), p. 205.
9. KOROLEV, N. V. AND AGROSKIN, L. S., *Biophysics*, 2, 501 (1957) (translated from the Russian by Pergamon Press).
10. WOLKEN, J. J. AND SCHWERTZ, F. A., *J. Gen. Physiol.* 37, 111 (1953).
11. RABINOWITCH, E. I., "Photosynthesis" (Interscience, New York, 1951), vol. 2, part 1.
12. WOLKEN, J. J. AND MELLON, A. D., *Biochem. et Biophys. Acta*, 25, 267 (1957).
13. STROTHER, G. K. AND WOLKEN, J. J., *Exp. Cell Res.*, in press.
14. DETWILER, S. R., "Vertebrate Photoreceptors," Macmillan, New York, 1953.
15. WALD, G. AND ZUSSMAN, H., *J. Biol. Chem.*, 122, 449 (1938).
16. WALD, G., *J. Gen. Physiol.*, 31, 377 (1948).
17. This work was aided by grants from the U. S. Public Health Service, National Institute of Neurological Diseases and Blindness (B-397-C5 and B-1874-A), and from the International Lions Club (14B).

G. K. STROTHER AND J. J. WOLKEN

NICOTINE ANALYSIS

Nicotine is widely distributed in nature, occurring in vegetables, fruits, berries and many leafy plants. One of the richest natural sources of nicotine is the tobacco plant, of which the burley variety usually exhibits the highest concentration of this alkaloid. Nicotine may also be found in the blood or tissue of animals after the ingestion of materials containing nicotine, or after the inhalation of smoke from these materials.

The analysis of nicotine in tobacco is im-

portant in the control of quality in cigarette manufacture. The AOAC modification¹ of Jensen and Haley's⁹ gravimetric silicotungstate method had been used for this analysis for many years. Because this method is tedious and time-consuming, other more convenient and rapid means have been sought for the routine determination of nicotine. In 1950, Willets *et al.*¹⁷ published a method for the determination of nicotine based on the ultraviolet absorption of nicotine hydrochloride at 259 $m\mu$. The alkaloid can be extracted or steam-distilled⁷ from an alkaline slurry of the tobacco. Chloroform appears to be the most popular solvent to be used for this extraction although many other water-immiscible liquids serve as well. The nicotine must be recovered from the solvent by extraction into dilute hydrochloric acid. If the alkaloid is steam-distilled, the distillate is passed directly into the dilute acid. Absorption measurements are made on this acid solution after it has been diluted to a suitable volume. Readings are taken at 259 $m\mu$ and on each side of this peak maximum, the latter readings being used to correct for background absorption.¹⁷ The concentration of nicotine in the sample is obtained from a standard curve prepared previously from known nicotine samples.

With proper modifications, the method of Willets *et al.* has been applied to the determination of nicotine in plant materials,⁴ fruits, vegetables, berries,^{13, 14} and tobacco smoke.^{5, 6, 8, 10, 11, 12, 16}

Early attempts^{6, 8} to apply the method of Willets to the determination of nicotine in tobacco smoke were not entirely successful because serious spectrophotometric background interferences were encountered. However, Laurene and Harrell¹¹ found that these interferences could be removed by a short steam-distillation of the acidic medium in which the smoke had been collected prior to the addition of alkali in the steam-distillation of nicotine. These workers succeeded in developing a rapid and accurate analysis of

nicotine in smoke. Wartman, Cogbill and Harlow¹⁶ improved the means of collecting the nicotine in cigarette smoke thus effecting an even greater saving in time for the analysis. The ultraviolet spectra of other alkaloids have been studied by Berman and Wright.²

A very sensitive spectrophotometric method for the determination of nicotine in blood has been devised utilizing the absorption of the cyanogen bromide- β -naphthylamine-nicotine complex at 420–540 $m\mu$.¹⁸

Because nornicotine accompanies and is measured as nicotine in all the accepted analytical methods, the specific determination of nornicotine may sometimes be necessary. Two spectrophotometric methods for the analysis of nornicotine are available.^{3, 15}

REFERENCES

1. Assoc. Offic. Agr. Chemists, "Official Methods of Analysis," 8th ed., p. 66, 1955.
2. BERMAN, E. AND WRIGHT, H. N., "Ultraviolet Photometric Identification of Alkaloids," *Arch. Ind. Hyg. Occupat. Med.*, **8**, 518–527 (1953).
3. BOSE, B. C., DE, H. N. AND MOHAMMAD, S., "Studies on the Biogenesis of Alkaloids in Tobacco Plants. Part II. Investigation on Transmethylation of Nicotine and Nornicotine in *N. Tabacum* and *N. Glauca*," *Indian J. Med. Research*, **44**, 91–97 (1956).
4. CROMWELL, B. T., "The Alkaloids," PAECH, K. AND TRACEY, M. V., "Modern Methods of Plant Analysis," Vol. IV, p. 367–516, Springer-Verlag, Berlin-Göttingen-Heidelberg.
5. ESCHLE, K., "Spectrophotometric Determination of Nicotine," *Mitt. Gebiete Lebensm. u. Hyg.*, **50**, 258–263 (1959).
6. FILK, H., STURMER, E. AND LOESER, A., "Investigation on the Amount of Nicotine in Cigarette Smoke," *Arzneimittel-Forsch.*, **4**, 367–368 (1954).
7. GRIFFITH, R. B., "The Rapid Determination of Total Alkaloids by Steam Distillation," *Tobacco Sci.*, **1**, 130–137 (1957).
8. GREENBERG, L. A., LESTER, D. AND HAGGARD, H. W., "The Absorption of Nicotine in Tobacco Smoking," *J. Pharmacol. Exptl. Therap.*, **104**, 162–167 (1952).
9. JENSEN, C. O. AND HALEY, D. E., "Studies on

- the Nicotine Content of Cigarette Smoke," *J. Agr. Research*, **51**, 267-276 (1935).
10. KRITZ, C. H. AND NEWSOME, J. R., "Quantitative Studies on Cigarette Smoke. III. Methods of Analysis for Filter Cigarettes," *Tobacco Sci.*, **2**, 14-19 (1953).
 11. LAURENE, A. H. AND HARRELL, T. G., "Improved Spectrophotometric Method for Determination of Nicotine in Tobacco Smoke," *Anal. Chem.*, **30**, 1800-1802 (1958).
 12. PLEASANTS, S. W., HAYNES, C. M. AND HARROW, L. S., "A Rapid Spectrophotometric Determination of Total Nicotine Alkaloids in Tobacco Smoke," *J. Assoc. Offic. Agr. Chemists*, **42**, 424-427 (1959).
 13. SCHWARTZMAN, G., "Report on Nicotine in Foods," *J. Assoc. Offic. Agr. Chemists*, **41**, 566-567 (1958).
 14. SCHWARTZMAN, G., "Report on Nicotine in Foods," *Ibid.*, **42**, 556-557 (1959).
 15. STEPHENS, R. L. AND WEYBREW, J. A., "Isatin: A Color Reagent for Nicotine," *Tobacco Sci.*, **3**, 48-51 (1959).
 16. WARTMAN, W. B., JR., COBELL, E. C. AND HARLOW, E. S., "Determination of Particulate Matter in Concentrated Aerosols. Application to Analysis of Cigarette Smoke," *Anal. Chem.*, **31**, 1705-1709 (1959).
 17. WILLETS, C. O., SWAIN, M. L., CONNELLY, J. A. AND BRICE, B. A., "Spectrophotometric Determination of Nicotine," *Anal. Chem.*, **22**, 430-433 (1950).
 18. WOLFF, W. A., HAWKINS, M. A. AND GILES, W. E., "The Spectrophotometric Estimation of Nicotine in Blood," *J. Biol. Chem.*, **175**, 825-831 (1948).

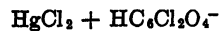
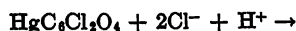
ANDERS H. LAURENE

SULFATE, CHLORIDE, AND FLUORIDE DETERMINATIONS WITH CHLORANILIC ACID

Introduction. The spectrophotometric determination of sulfate, chloride, and fluoride ions can be carried out with metal salts of chloranilic acid. The metal chloranilate, itself only slightly soluble, reacts with the desired ion to form an insoluble or slightly dissociated salt, and liberates the highly colored acid chloranilate ion. The color is proportional to the concentration of the desired ion. The solutions must be carefully buffered since the absorption of chloranilic acid solutions is dependent upon pH.

Interfering cations are removed with ion exchange resins. Sensitivity and selectivity are enhanced by proper selection of metal chloranilate, solvent, and pH.

Discussion. An interesting reaction discovered by Coutinko and Almeida⁵ suggested a new colorimetric method for determining chloride. It was found that the silver salt of chloranilic acid, added to a solution containing chloride ions, forms AgCl and releases the reddish purple acid-chloranilate ion, the spectrum of which may be measured colorimetrically. However, silver chloranilate is inconvenient for quantitative determinations because colloidal AgCl is produced. Methods based on the formation of HgCl₂ gave better results.^{8,7} Barney and Bertolacini¹ used a method based on the reaction



where the mercuric chloride formed is soluble, although only very slightly dissociated. Methyl "Cellosolve" is added to lower the solubility of mercuric chloranilate and to suppress the dissociation of mercuric chloride, and nitric acid is added to give maximum absorbance. Al, Fe, Ba, Ca, Cd, Sr, Cu, K, Mg, Mn, Pb, and Zn cations interfere by forming soluble complexes or precipitates with chloranilic acid.^{8,9} However, they are easily removed with the ion exchange resin.⁶ Bromide, iodide, iodate, thiocyanate, fluoride, and phosphate produce serious interferences.

Direct applications of the method include the determination of chloride in blood serum, wine, and waste waters. It should be adaptable to the determination of bromide, iodide, and thiocyanate because these ions form slightly ionized mercuric compounds.

The determination of sulfate is based on the reaction of solid barium chloranilate with sulfate.² A 50% ethyl alcohol solution is used to decrease the solubility of barium sulfate and barium chloranilate. Interfering cations are removed by ion exchange. Chlo-

ride, nitrate, bicarbonate, phosphate, and oxalate do not interfere at the 100 ppm level. The method has been applied to the determination of sulfate in water and of sulfur in petroleum products.

Fluoride is determined by reaction with strontium chloranilate in 50% isopropyl alcohol.⁴ Chloride, bromide, iodide, carbonate, oxalate, sulfate, and phosphate ions interfere.

When the absorption of chloranilic acid is measured in the ultraviolet region, the limit of detection is 0.06 ppm for sulfate, 0.05 ppm for chloride, and 5 ppm for fluoride. The detection limit for fluoride might be improved by the use of other metal chloranilates and other solvents.

Thorium chloranilate has been suggested lately¹⁰ as the basis of a sensitive spectrophotometric method for determining fluoride. In this method, fluoride reacts with thorium fluorochloranilate in buffered aqueous methyl "Cellosolve" probably to form both thorium fluorochloranilate and acid chloranilate ion. Most interfering cations can be removed with ion exchange resins. Sensitivity is controlled by proper combination of wave length and methyl "Cellosolve" concentration. The limit of detection is 0.01 ppm of fluoride in the original sample. The method has been tested by analyzing waters and catalysts.

REFERENCES

1. BARNEY, J. E. AND BERTOLACINI, R. J., *Anal. Chem.*, **29**, 1187 (1957).
2. BARNEY, J. E. AND BERTOLACINI, R. J., *ibid.*, **29**, 281 (1957).
3. BERGNANN, J. G. AND SANIK, J., *ibid.*, **29**, 241 (1957).
4. BERTOLACINI, R. J. AND BARNEY, J. E., *ibid.*, **30**, 202 (1958).
5. COUTINHO, A. B. AND ALMEIDA, M. D., *Anais. assoc. quim. Brasil*, **10**, 83 (1951).
6. FRITZ, J. S. AND YAMAMURA, S. S., *Anal. Chem.*, **27**, 1461 (1955).
7. IWASAKI, I., UTASUMI, S. AND OZAWA, T., *Bull. chem. soc. Japan* **25**, 226 (1952).
8. JOHNSON, W. C., ed., "Organic Reagents for

Metals," p. 22, Chemical Publishing Co., New York, 1955.

9. TYNER, E. H., *Anal. Chem.*, **20**, 76 (1948).

10. HENSLEY, A. L., AND BARNEY, J. E., *ibid.*, **32**, 828 (1960).

T. HADJIIOANNOU

TITRATION, SPECTROPHOTOMETRIC

The titration procedure, whereby an unknown quantity of a specific substance is determined by adding to it a standard reagent (the titrant) which reacts with it in a definite and known proportion, is well established as one of the most precise, accurate, rapid, and simple methods of quantitative analysis. Many stable titrants have been found which react rapidly and quantitatively either directly with a large number of sought-for constituents or with their products from prior quantitative reactions, thereby providing wide applicability. Of course, even with a good available reaction, whether it be acid-base, precipitation, redox or complexation, a reliable method of determining the end point is required; i.e. an experimental method which indicates to the chemist the quantity of titrant just sufficient to be chemically equivalent to the unknown quantity of sought-for constituent. The end point should be coincident with the equivalence point, although good accuracy can be obtained if there is a small reproducible difference (titration blank) between equivalence and end points.

At present there is not any one end-point system universally applicable for all the useful titrations. Consequently many different end-point systems have been developed and applied to provide good precision and accuracy for specific titration problems. In fact, one of the common classifications of titrations is according to the method of end-point detection. Hence, a *spectrophotometric titration* is one in which the end point is determined by measuring changes during the titration of absorbed radiation in a pre-selected wave length region. This is analogous

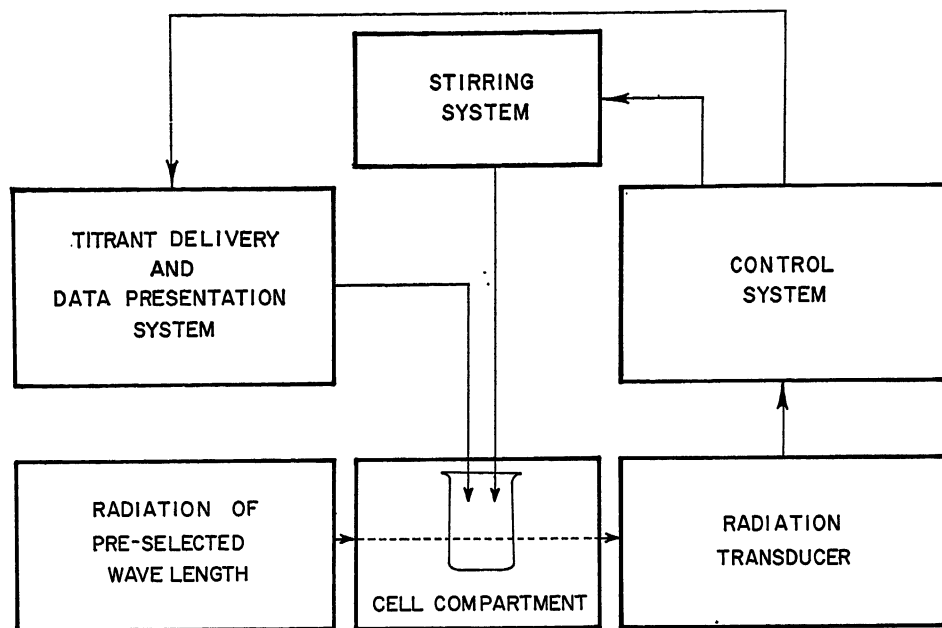


FIG. 1. Block diagram illustrating general experimental requirements for a spectrophotometric titration.

to potentiometric, conductometric, amperometric, turbidimetric, and thermometric titrations which are so designated because the end points are determined by measuring changes of potential, conductance, current, turbidity, and temperature, respectively. The characteristics of the spectrophotometric titration system make it one of the most versatile, sensitive and accurate methods for end-point detection.

Experimental Requirements for Spectrophotometric Titrations. The general experimental requirements for performing a spectrophotometric titration are illustrated by the block diagram, Figure 1. Assuming that a rapid and quantitative reaction is available between a titrant and the sought-for constituent, it is necessary to have a readily accessible band of radiation (in the visible, near UV or near IR) which is absorbed by either the titrant, sought-for constituent, reaction product or added indicator substance. Also, the selected radiation must not be completely blocked (absorbed or

scattered) by nonreacting constituents, particles in the sample or the titration cell, although it can be partially blocked. The selected band of radiation is focused through the sample in the titration cell and into a transducer which produces an electrical signal (voltage or current) related to the amount of radiation absorbed by the titration mixture. The electrical signal is monitored by the control system and the information used to terminate the titration at a suitable point. The titrant delivery system is constructed to be easily controlled and to present an accurate measure of the titrant delivered at any point. The cell compartment eliminates interference from room light and provides rigid support for the titration cells.

For a manual spectrophotometric titration a technician is part of the control system and operates the stirring and titrant delivery devices. Increments of titrant are added, mixed with the sought-for constituent, and a meter or dial observed which indicates the

magnitude of the signal from the radiation transducer. For some titrations the change of absorbed radiation is gradual. Therefore, readings (absorbance values) are obtained after addition of each increment of titrant and are plotted versus volume of titrant, and the end point determined from the titration curve. In other cases, the absorbing species undergoes a relatively large concentration change at the equivalence point. This produces a large change in meter reading which sharply delineates the end point, and the titrant delivery may be terminated exactly at the end point rather than plotting a titration curve.

The manual titrations require continuous technician time and for routine determinations become tedious, time consuming, and subject to personal bias. Consequently there have been many efforts in recent years to remove some or all of the titration manipulations from the hands of the technician. Partial or complete automation can now be accomplished by various electronic and mechanical components in the control system.

Spectrophotometric Titration Curves.

As previously noted a titration curve can be manually obtained by adding increments of titrant, taking meter readings at several volumes of titrant, and plotting absorbance versus volume. Also, the curve can be automatically recorded by synchronizing a motor-driven buret with the chart drive to provide a volume axis, and driving the recorder pen with an amplified and modified signal from the radiation transducer to provide an absorbance scale for the chart width.

Regardless of the method for obtaining the spectrophotometric titration curves their general shapes depend on the combination of titrant (T), sought-for constituent (S), reaction product (TS) and/or added indicator (Y) which undergoes changes of absorbance at the preset wave length during the titration. For any specific chemical reaction the general shape of the titration curve can be

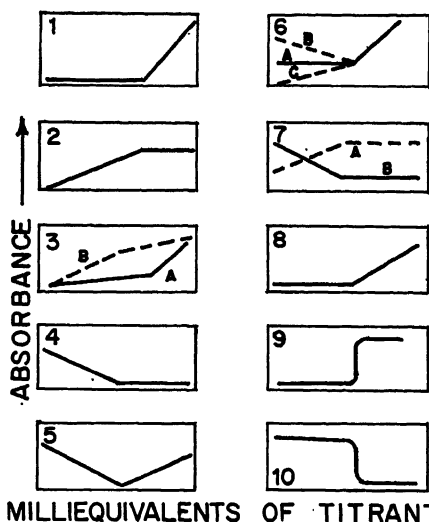


FIG. 2. General types of spectrophotometric titration curves.

altered by changing to a wave length where a different combination absorbs.

The various types of titration curves are given in Figure 2, Types 1-10. Types 1 through 7 are without and types 8 through 10 with added indicators. In all examples the given conditions are assumed to be true for a specific band of radiation, and dilution of the sample by the titrant assumed negligible.

The curve given for Type 1 is for the case where T absorbs, but S and TS do not absorb. An example of this is the titration of ferrous iron with permanganate titrant at a preset wave length in the region of 550 millimicrons. The ferrous iron and the reaction products when reacted with permanganate do not absorb significantly at this wave length but the titrant absorbs strongly.

If a solution containing a small amount of Cu^{++} ions is buffered and titrated with a standard EDTA titrant a curve similar to Type 2 can be obtained at a wave length of 260 millimicrons. In this case T and S do not absorb significantly at the preset wave length, but the reaction product (TS), the copper-EDTA complex, has a large absorptivity.

In Type 3, T and TS absorb and S does not absorb, but in 3A the absorptivity of the titrant is greater than that of the reaction product, and the reverse is true for Type 3B. The curve in Type 4 is quite common and results from absorption by S and essentially no absorption by T and TS . A V-shaped curve is a result of S and T absorbing and TS not absorbing as illustrated in Type 5. Several shapes of curves are obtained when T , S and TS all absorb, and these are illustrated in Types 6A, B and C. In 6A the absorptivity of TS is equal, in 6B less than, and in 6C greater than the absorptivity of S . Both S and TS absorb in Type 7, and T does not absorb, but the absorptivity of reaction product is greater than that of the sought-for constituent in 7A and less in 7B.

If neither T , S , or TS absorbs in an easily accessible wave length range, an indicator substance (Y) might be added to provide a spectrophotometric end point. One type of indicator substance does not absorb itself but combines with either the titrant, sought-for constituent or reaction product to form an absorbing species TY , SY or TSY , the concentration of which changes during the titration so as to give an end point. An interesting example of this type is the titration of a small quantity of Th^{+4} with EDTA using Cu^{++} as an added indicator. At easily accessible wave lengths none of these constituents absorbs, but the Cu-EDTA complex absorbs strongly at 260 millimicrons. The stabilities of the complexes are greatly different and the thorium is quantitatively complexed with EDTA before the copper is significantly complexed. Therefore, the absorbance remains constant until essentially all the thorium is complexed; then the titrant combines with copper to form the Cu-EDTA complex and the absorbance increases continuously as its concentration increases by adding more and more excess titrant. This example is illustrated as Type 8 in Figure 2, but curves somewhat similar to Types 4 and 2 might result if SY or TSY were the only absorbing species.

In all the above titration curves the end points are found by the intersection of two straight lines and are similar in this respect to conductometric and amperometric titration curves. In contrast, Types 9 and 10 are quite similar in shape to potentiometric titration curves and are typical for added indicators which exist in one structural form before and another form after the equivalence point, and where one form absorbs most strongly at the preset wave length. Nearly all classical visual color indicators for aqueous and non-aqueous acid-base, redox, and complexation titrations give curves of these two types. At the equivalence point a small increment of titrant produces a large change of either pH, redox potential, or pM which causes a large concentration change for one form of the indicator. In Type 9 the form of the indicator with the highest absorptivity at the preset wave length suddenly increases in concentration at the equivalence point, giving a large increase of absorbance. In Type 10 the concentration of the absorbing form suddenly decreases and the absorbance decreases. These large changes of absorbance can be readily detected by the eye if the absorption bands are in the visible, as with the classical visual indicators. However, selected wave lengths of radiation and photocell detectors provide a combination which is more sensitive and selective and also suitable at wave lengths outside the sensitivity range of the eye. The number of indicator materials that can be applied is greatly increased and only a narrow transmission band is necessary when the sought-for constituent is in a nearly opaque solution (caused by the presence of many radiation absorbing constituents which do not interfere with the titration reaction).

The output electrical signals from the light detector for Types 9 and 10 are more convenient for automation of the titration than Types 1 through 8, although the latter can be used. All titrations presently using visual absorption indicators, as well as the many others that can give curves similar to

Types 1-10, can be performed by either manual or automatic spectrophotometric end-point detection.

Instrumentation. Conventional spectrophotometers and filter photometers can be used to provide the end-point signals for spectrophotometric titrations. However, they are generally quite cumbersome after the other titration equipment is mounted in position and do not provide the versatility often desired. Therefore, new instruments have been specifically designed and produced for spectrophotometric titrations. All the components are integrated with convenient mounting of titrant delivery systems, efficient stirring, simple and rapid insertion and removal for many sizes of titration beakers, and direct connections to suitable control systems for automatic end-point termination or recording of the titration curve. The titration cells can be ordinary "Pyrex" beakers in the visible and down to 350 millimicrons in the ultraviolet, and quartz beakers can be used below 350 $m\mu$.

The usual method for obtaining the necessary bands of radiation is with a continuous source of radiation and a monochromator. Prisms and gratings can be used but interference filters are less expensive and can provide narrow bands (10 to 15 millimicrons half-width) of radiation in the visible, near UV and near IR. In certain cases better selectivity and sensitivity might be obtained by use of a monochromatic light source such as a gas discharge lamp.

The titrant delivery system can be an ordinary stopcock buret, preferably with self-zeroing and refill devices, or one of the new automatic burets. In one of these the titrant is forced through a tube with a precision-ground plunger driven by a motor. The movement of the plunger and volume of titrant delivered are determined from the number of revolutions by the motor. The plunger and gear system can be made so that a revolution counter reads directly in milliliters, and very high accuracy is possible even for small volumes.

In certain cases it is possible to generate electrolytically the titrant at a suitable generator anode or cathode, and the milliequivalents of titrant delivered can be determined by automatically integrating the current from the start of the titration to the end point and applying Faraday's Law. The data presentation system can be made to show the titration result directly in numbers on a dial or printed tape.

Accuracy. The relative reproducibility and accuracy of spectrophotometric titrations is often of the order of 0.1%. This is possible because many good procedures have been developed whereby interferences have been eliminated, and the quantity of titrant added for a specific sample is sufficient so the accuracy of the titrant delivery system is not a limiting factor. The accuracy by spectrophotometric titration compares very favorably with conventional absolute spectrophotometric measurements which seldom are more accurate than 1% because of various solution and instrumental phenomena. For example, quantitative results for samples of low absorbance can be inaccurate because of imperfections or dust and dirt on the sample cell windows; samples of high absorbance can be in error because of stray light in the instrument. Unsuspected impurities absorbing at the same wave lengths as the sought-for constituent or solution turbidity can cause large relative errors. Whereas these phenomena cause changes of absolute absorbance they merely produce a shifting of the titration curve on the absorbance axis and do not significantly affect the end point within certain practical limits.

In general, for many applications the titration procedure is unsurpassed for simplicity and accuracy among quantitative measurement methods. In other cases the sample preparation, (i.e. dissolution of sample and elimination of interferences) is sufficiently time consuming and subject to errors so as to make titrations impractical.

When it is a matter of choosing the end-point method for a specific titration many

things must be considered, but certainly the spectrophotometric system (with its versatility, sensitivity, accuracy and simplicity for automation) should always be near the top of the list along with potentiometric and amperometric end-point methods.

H. V. MALMSTADT

ULTRAMICROSPECTROPHOTOMETRY

Ultramicrospectrophotometry refers to spectrophotometry using samples of the size encountered in ultramicroanalysis, i.e. 10^{-6} gm or smaller. In practice, the distinction between *micro*spectrophotometry and *ultra*-*micro*spectrophotometry is not always clear, since biologists and others working with histologic preparations commonly refer to absorption measurements on individual cells, or parts thereof, as microspectrophotometry. In such instances, the sample being studied may be considerably below the limit given for ultramicrospectrophotometry, as for example when the hemoglobin spectrum is determined on a single erythrocyte containing approximately 3×10^{-11} gm hemoglobin.

The major problem in chemical ultramicrospectrophotometry has to do with design of a cell that possesses a sufficiently small cross sectional area to give good absorption intensities and yet transmits sufficient energy to permit accurate photometry. Several cell designs have been used. By constructing the cell from capillary tubing, it is possible to obtain path lengths of several cm and internal diameters smaller than 1 mm, although cells of larger cross section are more convenient to use. Such cells must be illuminated with parallel light and the energy limitation imposed by the small aperture requires a sensitive photometer or increase in optical slit width, or both. Craig, Bartel and Kirk¹ have described a 5-cm capillary cell of 20 μ l volume, as well as a cell holder and special photomultiplier photometer, for use with the Beckman DU spectrophotometer.

In favorable situations, this permits absorption measurements on samples as small as 10^{-10} gm.

Cells that are more convenient to use, although optically less efficient, were designed by Lowry and Bessey.² These cells have 10 mm path lengths and possess rectangular cross sections that measure 1 mm or 2 mm in width by 25 mm in height. The height can be reduced by appropriate masks to a minimum of about 2.5 mm. Visible and ultraviolet absorption measurements on samples in the 10^{-7} to 10^{-9} gm range can be made with cells of this type using a Beckman DU spectrophotometer.

The development of electronic ordinate expansion and of beam condensing optics for use with modern recording spectrophotometers (such as the Perkin-Elmer Model 4000A) permits a 5–10 fold increase in sensitivity in measurements with cells of the Lowry type. Electronic ordinate expansion is difficult with long-path capillary cells because of energy limitations, and with these cells beam condensing optics cannot be used to increase energy because of the highly convergent rays that exist in such systems.

Mason³ has recently described use of KBr micropellets for ultramicrospectrophotometric measurements. The sample must have a sufficiently low vapor pressure to permit its incorporation into KBr either by grinding or by lyophilization. KBr pellets are pressed with standard micro-dies of the type used in infrared spectrophotometry. Using KBr micropellets of 0.5 mm diameter and weighing 0.5 mg, an O.D. of 0.05 was obtained with 2×10^{-9} gm of safranin at 520 m μ . This is equivalent to the calculated value for a 20 μ l capillary cell having 5 cm path length, and 10-fold better than the calculated value for a 30 μ l Lowry cell having 1 cm path length. Due to the short path (less than 1 mm) through the pellet, it is possible to use a highly convergent beam and attain sufficient energy for ordinate expansion. This

permits a further 5-10 fold reduction in sample.

Sample requirements for spectrophotometry in the infrared are much larger than in ultraviolet and visible regions due to weaker absorptions, and infrared ultramicrospectrophotometry has barely been achieved. Coates, Offner and Siegler⁴ have published spectra obtained with an infrared microscope on 10^{-6} gm amounts of cholesterol in CS_2 and on single textile fibers weighing 10^{-7} gm. Infrared spectra on microgram amounts of steroids have been obtained by the KBr micropellet technique.⁵ A good summary of problems encountered in infrared microspectrophotometry is given by Wood.⁶

REFERENCES

1. CRAIG, R., BARTEL, A. AND KIRK, P. L., "A Photometer and Absorption Cell Attachment for Ultramicrospectrophotometry," *Rev. Sci. Inst.*, **24**, 49 (1953).
2. LOWRY, O. H. AND BESSEY, O. A., "The Adaptation of the Beckman Spectrophotometer to Measurements on Minute Quantities of Biological Materials," *J. Biol. Chem.*, **163**, 633 (1946).
3. MASON, W. B., "Ultraviolet and Visible Ultramicrospectrophotometry Using KBr Pellets," The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., March 1959.
4. COATES, V. J., OFFNER, A. AND SIEGLER, E. H., "Design and Performance of an Infrared Microscope Attachment," *J. Optical Soc. Am.*, **43**, 984 (1953).
5. MASON, W. B., "Infrared Microsampling in Bio-Medical Investigations," Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1958.
6. WOOD, D. L., "Infrared Microspectroscopy in Biological Research," *Ann. N. Y. Acad. Sci.*, **69**, 194 (1957).

W. B. MASON

VACUUM ULTRAVIOLET REGION INSTRUMENTATION

Introduction. The vacuum ultraviolet portion of the electromagnetic spectrum extends from 2000 Å to 1 Å. The difference be-

tween the conventional and vacuum ultraviolet is arbitrary and is usually distinguished by the experimental techniques employed in each region. This region has been thoroughly reviewed by Lyman¹³ and Inn.⁸

In 1893 Schumann made the first investigation of this region and reached 1200 Å as a lower limit.² The introduction of the concave grating by Lyman in 1906 enabled the limit to be extended to 500 Å. This limit was further lowered by the improvement of existing sources, but it was not until 1925 when Compton and Doan introduced the use of a grating at grazing incidence that wavelengths lower than 100 Å could be obtained.

The optical transitions encountered in the vacuum ultraviolet are of the order of 6 e.V. or more as compared to about 4 e.V. encountered in the conventional ultraviolet. Since the ionizational potential of most molecules lies around 6 e.V., electronic transitions from the ground state of the neutral molecule to the molecular ion are most often observed in the vacuum ultraviolet. These transitions are known as Rydberg transitions.

General Instrumental Problems. The two main instrumental difficulties which are encountered in this region are: the absorbance of air, and the unavailability of transparent substances for use in optical systems. The interference of air is due to the absorption of oxygen in the region 1950 Å to 2 Å. This problem is usually eliminated by evacuating the system to 1 μ .

Calcium fluoride,¹⁴ lithium fluoride¹⁶ and sapphire⁴ have been used for making the optical accessories for the region from 2000 to 1100 Å. However, the use of such materials makes it impossible to work below 1100 Å because of their increasing absorbance. Recently thin films of silicon monoxide, aluminum and beryllium¹ have been used both as filters and cells for wavelengths shorter than 1000 Å, but the techniques

necessary with such films have not yet been fully developed.

Light Sources. The availability of good light sources has long been a problem in the vacuum ultraviolet. It has been found desirable to use a background light source which has a strong continuum in the region of interest, is continuously operating and is stable over reasonable periods of time. The hydrogen discharge tube, especially as modified by Lyman and others,^{9, 22} fulfills these requirements. The Lyman source consists of a discharge through a thick-walled, open-ended capillary tube. The radiation is obtained by viewing the tube down the length of the bore of the tube. The discharge gas is usually hydrogen for absorption studies, but in emission work the substance to be studied is used as the discharge medium.

The helium continuum from 600 to 1000 Å has also been used; however, it is too unstable to be used in spectrophotometric studies. Recently the continuous molecular-emission spectra of xenon, krypton, argon and neon^{20, 21} have been used in the Schumann region from 790 Å to 2000 Å with great success. The spectrum of these rare gases is produced by microwave energy. The stability of these sources makes them extremely useful for spectrophotometric work.

The low pressure spark¹² and other spark sources have often applied to the determination of absorption coefficients because of their constant intensity. Their main disadvantage is a relatively short life time.

Vacuum Monochromators. For use in the longer wavelength portion of the vacuum ultraviolet, prism instruments have been widely used because of their low cost and ease of construction. Their construction is identical with those used in the conventional ultraviolet. However, scattered light is a very important problem in the vacuum ultraviolet. Often the light in the near ultraviolet and visible regions scattered from the face of a prism is of much greater intensity than the dispersed radiation. This is especially important in spectrophotometric de-

terminations, and various methods have been used to correct for it. The most successful method of eliminating this scattered radiation has been developed by Hammond and Price.⁵ It consists of vibrating a Littrow mirror through a small angle around a horizontal axis while the spectrum is being scanned by rotating the prism-mirror combination about a vertical axis. By means of an amplifier tuned to the vibration frequency of the mirror, the scattered radiation is neglected by the detecting device.

Grating instruments fall into two general categories: those that employ normal incidence and those that employ grazing incidence. Both methods of incidence use the concave grating because of the greater dispersion and resolution obtainable. Incidence angles are approximately 14° for normal incidence and may extend to 89° for a grazing incidence instrument.

The efficiency of grating instruments is seriously impaired by the decrease in reflecting power with a decrease in wavelength. This is especially true at normal incidence. Sabine¹⁵ conducted an extensive survey on the reflecting power of various materials in the vacuum ultraviolet. His results show that platinum and aluminum are the best reflectors in this region. Various methods of improving the reflectivity of a grating have been attempted; the most successful employs the platinizing of aluminum surfaces.¹⁹

The vacuum spectrograph as developed by Tousey *et al.*¹⁸ and manufactured by Baird has proved the most versatile instrument for work in this field.

Vacuum Ultraviolet Detectors. Specially prepared photographic emulsions¹⁷ and oil sensitized emulsions⁶ have been used almost exclusively for precise wavelength measurements and for the analysis of various spectra. However, recently photomultiplier detectors,⁹ photoelectric cells⁸ and windowless vacuum photoelectric cells⁷ have been developed for use in this region. The latter type especially shows promise because of the very high quantum efficiency in this

region of the spectra. All these electronic detectors are usually standardized against a standard thermocouple.

Applications. Thus far the vacuum ultraviolet has not often been used as a method of chemical analysis because of the instrumental difficulties encountered in this region and especially because of the lack of good solvents¹¹ which are transparent in this region at the lower wavelengths. The absorption coefficients of many substances have been measured and used for the determination of impurities in gases. In a survey of the spectra of pure hydrocarbons, Jones and Taylor¹⁰ noted that this region would be more useful for the determination of the total concentration of all members of a group of compounds with similar electronic structure than for distinguishing between individual members.

In other fields, especially those of substitution effects and electronic structure, vacuum ultraviolet spectroscopy has proved more successful.⁸ Increasingly more convenient experimental techniques will lead to a more widespread application and a greater knowledge of the electronic nature of many compounds.

REFERENCES

1. ASTOIN, N. AND VODAR, M. B., *J. Phys. Radium*, **14**, 424 (1953).
2. BOYCE, J. C., *Revs. Mod. Phys.*, **13**, 1 (1941).
3. CHUBB, T. A. AND FRIEDMAN, H., *Rev. Sci. Instr.*, **26**, 493 (1955).

4. FRIED, S., McMURRAY, H. L. AND ROSENBAUM, E. J., *J. Chem. Phys.*, **7**, 853 (1939).
5. HAMMOND, V. J. AND PRICE, W. C., *J. Opt. Soc. Am.*, **43**, 924 (1953).
6. HARRISON, G. R. AND LEIGHTON, P. A., *Ibid.*, **20**, 313 (1930).
7. HINTEREGGER, H. E. AND WATANABE K., *Ibid.*, **43**, 604 (1953).
8. INN, E. C. Y., *Spectrochim. Acta*, **7**, 65 (1955).
9. JOHNSON, F. S., WATANABE, K. AND TOUSEY, R. J., *J. Opt. Soc. Am.*, **41**, 702 (1951).
10. JONES, L. C. AND TAYLOR, L. W., *Anal. Chem.*, **27**, 228 (1955).
11. KLEVENS, H. B. AND PLATT, J. R., *J. Am. Chem. Soc.*, **69**, 3055 (1947).
12. LEE, P. AND WEISSLER, G. L., *J. Opt. Soc. Am.*, **42**, 80 (1952).
13. LYMAN, T., "The Spectroscopy of the Extreme Ultraviolet," 2nd ed., Longmans Green and Co., London, 1928.
14. POWELL, W. M., JR., *Phys. Rev.*, **45**, 154 (1934).
15. SABINE, G., *Ibid.*, **55**, 1064 (1939).
16. SCHNEIDER, E. G., *Ibid.*, **49**, 341 (1936).
17. SCHOEN, A. L. AND HODGE, E. S., *J. Opt. Soc. Am.*, **40**, 23 (1950).
18. TOUSEY, R., JOHNSON, F. S., RICHARDSON, J. AND TORAN, N., *Ibid.*, **41**, 696 (1951).
19. WATANABE, K., *Ibid.*, **43**, 318 (1953).
20. WILKINSON, P. G. AND TANAKA, Y., *Ibid.*, **45**, 344 (1955).
21. WILKINSON, P. G., *Ibid.*, 1044 (1955).
22. WORLEY, R. E., *Rev. Sci. Instr.*, **13**, 67 (1942).

EDWARD O. SHERMAN, JR.

VAPORS. See INFRARED SPECTROPHOTOMETRY (VAPOR SPECTRA, p. 577.)

BAND SPECTROSCOPY*

THEORY, INSTRUMENTATION, INTERPRETATION, AND APPLICATIONS

The term "band spectrum" is used to designate a spectrum originating either by emis-

sion or absorption in the molecules of a compound. As such it is to be distinguished from a line-spectrum, which is the designation of a spectrum originating in the atoms of a chemical element. It should not be assumed that the appellation band spectrum is necessarily descriptive. It is to be considered mainly of historical significance origi-

* Revision of article in the "Encyclopedia of Chemistry Supplement," Reinhold, New York, 1958, p. 34.

nating at a time when low dispersion instruments were generally used for observation, which imparted an appearance of unresolved bands to many of these spectra. Actually, if an exception is made of pure rotational spectra in the far infrared region, all band spectra are highly complex when observed under high resolution. The optical radiant energy identified with molecular spectra is distributed over a very wide range of frequencies extending from the ultraviolet to the far infrared, in effect joining the microwave region at wavelengths of the order of 1 mm. The dynamic conditions accounting for this distribution will be examined briefly.

The essential differences between atomic and molecular spectra are accounted for by the fact that the former are completely explained by quantized changes in the energy associated with the outer electronic structure, whereas the latter include not only this energy, but also contributions of energy resulting from the vibration of the component atoms relative to each other and from rotation of the molecule as a whole about an axis through the center of gravity. The actual energy pattern may be represented by a summation of these three contributions; that is, we may write $E = E_e + E_v + E_r$, or following the usual notation when the energy is expressed in wave number units or term values, $T = T_e + G + F$. All three forms of energy are quantized, but it may be shown that in some cases vibrational frequencies are the same as those predicted by classical mechanics. It is not necessary that all three forms of energy be present. There are instances of pure rotational energy. Since this energy is relatively small, such band spectra are found only in the far infrared beyond 20 microns.

Probably the outstanding example of a completely described rotational spectrum is to be found in the paper dealing with water vapor by Randall, Dennison, Ginsberg, and Weber.¹ Vibrational spectra with rotational structure are also of frequent occurrence.

Owing to the magnitudes of interatomic forces these are found in general between 3 and 15 microns.

Beginning with the observation of rotational fine structure of H_2O vapor by Eva von Bahr in 1913 and the subsequent observation of the same spectrum and those of the halogen acids by Sleator and Imes^{2, 3} a short time later, the quantum interpretation of band spectra developed rapidly. The body of information on this subject is remarkably complete. It may be stated safely that all observable features of well-resolved spectra of molecules in the vapor state may be completely accounted for both within the framework of classical quantum theory and that of wave mechanics.

The most complete discussion is to be found in two books by Herzberg.^{4, 5} The notation introduced in the following sections follows for the most part that employed by Herzberg. A fairly detailed treatment has been given by Ruark and Urey.⁶ Attention is also called to review articles by R. S. Mulliken⁷ and by D. M. Dennison.⁸ As the development of the subject is lengthy and detailed, only a few basic concepts are included here. In general the theory is built up by extensions of these ideas.

In the development of the quantum theoretical explanation of the detailed features of molecular spectra it is customary to begin with the spectra of diatomic molecules. This introduces a relatively greater degree of simplicity because one is dealing essentially with a two-body problem. Furthermore the full details of diatomic spectra are frequently completely observable, whereas the complexity of the spectra of polyatomic molecules is in general so formidable that the details may be resolved in relatively few instances, usually where considerations of symmetry permit a simplification of the model. The general features of polyatomic molecules may be explained by extending the concepts developed for diatomic molecules.

A physical model may be conceived for the

diatomic molecule which closely represents its actual features and properties. It is thought of as a dumbbell structure. First we think of it as a rigid rotator with an axis through the center of mass perpendicular to the line joining the nuclei of the constituent atoms. A wave-mechanical treatment of this rotator leads to the following expression for the quantized energy:

$$E_{\text{rot}} = J(J+1) \frac{h^2}{8\pi^2 I}$$

where h is Planck's constant, I is the moment of inertia and J is the rotational quantum number which can take a series of integral values 0, 1, 2, ... This formula is generally written $F(J) = BJ(J+1)$ where the constant

$$B = \frac{h}{8\pi^2 cI}$$

Each rotational energy state is characterized by one of these J values. The quantum mechanics also leads to a requirement for a selection rule for transitions between energy states $\Delta J = \pm 1$. Since such transitions account for the emission or absorption of spectral lines the frequency of such lines is given by

$$\nu = F(J+1) - F(J)$$

or

$$\nu = 2B(J+1); \quad J = 0, 1, 2, \dots$$

This leads to a series of equidistant lines. Such spectra are actually observed in the far infrared. The actual frequency of rotation of the rigid rotator may also be derived and turns out to be

$$\nu_{\text{rot}} = c2B\sqrt{J(J+1)} \approx c2BJ.$$

That is, for any state characterized by J the rotational frequency is approximately equal to the frequency of the spectral line that has this state as its upper state. Actually the molecule is not strictly rigid. A correction of the simple formula is necessary to account

for modification of the observed spectral features resulting from centrifugal stretching. The effect is tied in with the vibrational frequency of the molecule and leads to a modified expression for the rotation energy $F(J) = BJ(J+1) - DJ^2(J+1)^2$, where $D = (4B^3/\omega^2)$, ω being the vibrational frequency. This extra term is always small.

The dumbbell model is next considered as a harmonic oscillator, characterized by a simple harmonic motion of the constituent atoms along the line joining them under Hooke's law forces. Since the observed spectral frequency is in some instances equal to the classical vibrational frequency of a molecule of the described configuration, it is of interest to recall the formula for simple harmonic motion

$$\nu_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

where k is the force constant or force required to produce unit displacement, and m is the mass of the point moving with simple harmonic motion. For the model under consideration consisting of mass points, m_1 and m_2 , m is replaced by the reduced mass μ , equal to $m_2 m_1 / m_1 + m_2$. On the classical theory, only one vibration frequency is possible. The solution of the Schrödinger wave equation for the harmonic oscillation leads to the following equation specifying the vibrational energy states:

$$E(v) = h\nu_{\text{osc}}(v + \frac{1}{2})$$

where v is the vibrational quantum number that takes integral values 0, 1, 2, ... Transforming to term values the equation becomes

$$G(v) = \frac{\nu_{\text{osc}}}{c} (v + \frac{1}{2})$$

or

$$G(v) = \omega(v + \frac{1}{2})$$

where ω is the vibrational frequency in cm^{-1} . We thus obtain a series of equally spaced energy levels. The quantized emitted or ab-

BAND SPECTROSCOPY

sorbed energy in cm^{-1} takes place respectively by a transition from a higher to a lower or a lower to a higher vibrational state. The wave number characterizing such a transition is given by

$$\nu = G(v') - G(v'')$$

where v' and v'' are the vibrational quantum numbers of the upper and lower states respectively. The selection rule that governs such transitions and which also has been accounted for by quantum mechanics is

$$\Delta v = v' - v'' = \pm 1$$

It may be noted immediately that

$$\nu = G(v + 1) - G = \omega,$$

indicating that the quantum-mechanically derived frequency is equal to the classical frequency for all transitions. Thus we are led to expect a single vibrational absorption or emission band. Actually weak harmonics of approximately integral multiples of the fundamental frequency are sometimes observed, corresponding to transitions with Δj greater than 1. The reason for the appearance of harmonics is that there is an anharmonicity introduced into the oscillating system owing to the fact that the interatomic forces depart somewhat from Hooke's law both on close approach and extreme separation approaching dissociation. This leads to a breakdown of the selection rule. The correction for anharmonicity is in general relatively small.

The complete expression for the vibrational energy expressed as a term value is a power series including a quadratic and for extremely precise representation of wave numbers a cubic term in powers of $(v + \frac{1}{2})$. Thus we have

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 \dots$$

where the subscript e refers to the equilibrium position. Neglecting the cubic term we obtain

$$\Delta G_{v+1/2} = \omega_e - 2\omega_e x_e - 2\omega_e x_e v \dots$$

It is convenient to measure the levels from the zero point energy obtained setting $\nu = 0$. In this case $\Delta G = \omega_0 - \omega x_0 - 2\omega x_0 v$.

It is prerequisite to the emission or absorption of energy that the fundamental vibration cause a change in the electric dipole moment of the molecule; otherwise it is "infrared inactive." Illustrative of such inactive vibrations are those of diatomic molecules containing identical atoms such as O_2 or N_2 . In certain instances, inactive vibrations are observable as Raman effect displacements. Infrared and Raman effect observations therefore supplement each other advantageously.

The simultaneous occurrence of vibrational and rotational transitions accounts for the observed features of infrared spectra illustrated by those of the halogen acids.

The formulation may be summarized by combining the equations already given. The term value of the vibrating rotator becomes

$$T = G(v) + F_v(J) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \dots + B_v J(J + 1) - D_v J^2(J + 1)^2 + \dots$$

From this we obtain the abbreviated form of the expression for the wave numbers neglecting the correction for centrifugal stretching:

$$\nu = \nu_0 + B_v' J'(J' + 1) - B_v'' J''(J'' + 1)$$

where the values of B are appropriate to the respective vibrational states and take into account the interaction between rotation and vibration. If we set $\Delta J = +1$ and $\Delta J = -1$, respectively, and replace J'' by J the above equation reduces to the following two:

$$\nu_R = \nu_0 + 2B_v' + (3B_v' - B_v'')J + (B_v' - B_v'')J^2; \\ J = 0, 1, \dots;$$

$$\nu_P = \nu_0 - (B_v' + B_v'')J + (B_v' - B_v'')J^2; \\ J = 1, 2, \dots$$

These formulas represent two series of lines which are called the P and R branches. If the vibrations were strictly harmonic and if there were no centrifugal stretching accompanying the rotation or interaction between vibra-

tions, the branches of the band would consist of equally spaced lines extending each direction from the zero energy position of the vibration band. Actually taking these effects into account the *P*-branch shows a gradual increase in the separation of components and the *R*-branch a decrease.

Up to this point only cases have been considered where the electronic state of the molecule remains constant during the occurrence of vibrational and/or rotational transitions. A large class of bands, mostly in the visible and ultraviolet regions, is accounted for by a change in electronic energy, similar to that responsible for line emission spectra, accompanied by vibrational and rotational transitions. The electronic energy represents the largest contribution and accounts for the spectral location. These bands are characterized by recurrent regularities known as progressions. A rotational fine structure is superposed on the regularities. A good example is the CN bands which occur in emission with great intensity in the carbon arc. The electronic levels are characterized by vibrational structure which in turn have rotational fine structure. There is no strict selection rule for the vibrational transitions, that is, a transition can occur between any vibrational level of one electronic state and all the vibrational levels of the other. The set of bands arising from such a group of transitions forms a progression. Similarly each of these vibrational transitions is accompanied by rotational transitions yielding the usual *P* and *R* branches and in addition a *Q* branch resulting from $J'' - J' = 0$. This new selection rule is accounted for by theory, based on the fact that there is a difference in the angular momentum associated with the upper and lower electronic states.

The explanation of the features of the spectra of polyatomic molecules is developed naturally from the principles outlined for diatomic molecules. Instead of a single mode of vibration a polyatomic molecule possesses several determined by point group theory.

For a molecule of N atoms there are $3N - 6$ possible modes of vibration ($3N - 5$) for a linear molecule. A fundamental radiation frequency would be expected for each of these modes. Some however are inactive, as for instance the totally symmetric vibration of a linear symmetric molecule such as CO_2 . Except for what is described as a spherical top molecule there are always several moments of inertia corresponding to various possible axes of rotation. In general there is always a possibility of angular momentum about an axis of symmetry. This results in an extension of the selection rule for rotational quantum numbers to $\Delta J = 0$ in addition to $\Delta J = \pm 1$. There is a *Q* branch in these instances. An exception is the linear molecule. For example a CO_2 band shows no *Q* branch. As in the case of diatomic molecules a change in dipole moment is required for emission or absorption of energy.

Even moderately complex molecules show large numbers of vibration bands, either fundamentals or in general less intense overtone or combination bands. The rotational structure is resolved only in a few instances of relatively simple molecules where the available optical resolution can be brought to bear advantageously. Examples are CO_2 , CH_4 , and NH_3 . The observed absorption bands are in general envelopes that include the rotational energy accompanying the vibrations. Most of them occur in the "rock-salt region" between 2 and 15 microns. As may be expected, some modifications in the structure of a spectrum occur when the material is in the liquid or solid state.

Molecular Spectra. The spectrum of a molecule or an atom has been described as its most definitive characteristic. The fact that the spectrum is unique leads, of course, to applications in identification and analysis that are extremely useful and important. The term "finger-printing" of molecules is of course familiar to all analysts. The spectrum not only establishes the identification of compounds but distinguishes between vari-

ous types of stereoisomerism including cis- and trans-forms. In order to make the best use of spectra for identification, extensive libraries of spectral absorption curves have been assembled and are being extended. Among the first to attract widespread attention was the compilation by Barnes, Gore, Liddel, and Williams.⁹ An extensive set of spectra of hydrocarbons now numbered in the thousands represents a continuing effort by the American Petroleum Institute.¹⁰ A more recent program covering a wider range of chemical compounds is that sponsored by the Coblenz Society. The material collected by the organization is published and distributed by Sadtler.¹¹

The utilization of infrared analytical methods has become an important tool for industrial research, particularly in support of those industries dealing with petroleum products, plastics, and organic chemicals. The manufacture of spectrophotometric equipment is of itself an important industry. The developments in this field have been covered by biennial survey articles in *Analytical Chemistry*. The survey articles in the infrared field, including extensive compilations of references, were initiated by Barnes and Gore¹² and continued by Gore.¹³ This series provides an essentially complete index to current literature.

It was suggested by Coblenz more than half a century ago that the various radicals or structural elements of a molecule should contribute characteristic features to the absorption spectrum and that it might be possible to identify compounds on the basis of a synthesis of such features. The argument has considerable validity, but is not entirely conclusive. Several correlations of atomic groups and absorption frequencies in the form of charts are available.

The first was that of Barnes, Gore, Stafford and Williams,¹⁴ published in 1948. The well-known Colthup¹⁵ Chart was published in 1950. "Infrared Determination of Organic Structures," by Randall, Fowler, Fuson, and

Dangl,¹⁶ is largely devoted to a correlation of spectral features with various types of bonding. It also contains a compilation of spectra in chart form. The use of spectral data has made possible the identification and determination of properties of many short-lived molecules or free radicals. Examples are C_2 , CH , and NH .

Many physical and chemical properties of molecules can be inferred from spectral data. The representation of a vibration frequency by a Hooke's law formula is recalled. Knowing the masses of the constituent atoms and the frequency it is simple to derive the force constant associated with a given type of bonding and from this the heat of dissociation. Conversely, from a knowledge of bond strengths the location of the fundamental frequencies may be predicted. The rotational structure permits calculation of the moments of inertia and derivation of interatomic distances. Interesting features of geometry or spatial configuration may be established. For instance, the regular spacing of the rotational components of the CO_2 bands proves that it is a linear molecule. Similarly it has, in the instance of the water molecule, been possible to compute the angle at the O atom between the bonds connecting it to the two hydrogens.

Band spectra are important for the identification of isotopes and hence useful in the detection of rare products from reactors. The isotope effect, due to the presence of Cl^{37} along with Cl^{35} , was first observed by Imes³ and later demonstrated under high resolution by Meyer and Levin.¹⁷ The isotope effect is very large in the instance of deuterium substitution for hydrogen because of the large effect on the reduced mass of doubling the mass of one of the component atoms. It is of interest to compare the positions of the ν_2 and ν_3 fundamentals of H_2O and D_2O . The frequencies are as follows:

	H_2O	D_2O
ν_2	1595	1179
ν_3	3756	2789

This has interesting possibilities for analytical procedures where a region of interest might be obscured by the presence of water or in certain instances its use as a solvent.

A final statement concerns the astrophysical significance of band spectra. Since only optical radiant energy is a requirement without the necessary possession of the emitting sample, spectra may be used for a study of the atmospheres of planets or envelopes of stars. It is in this way that the presence of ammonia and methane in the atmosphere of Jupiter has been demonstrated.

A very recent and timely contribution to our knowledge of the constitution of planetary atmospheres is the recently reported work of Kiess, Corliss, and Kiess¹⁸, which leads to the conclusion that the atmosphere of Mars is composed principally of oxides of nitrogen. These findings have significant bearing on the question of possible life on that planet.

REFERENCES

1. RANDALL, H. M., DENNISON, D. M., GINSBURG, N., AND WEBER, L. R., "The Far Infrared Spectrum of Water Vapor," *Phys. Rev.*, **52**, 160 (1937).
2. SLEATOR, W. W., "Absorption of Infra-red Radiation by Water-Vapour," *Astrophys J.*, **48**, 125 (1918).
3. IMES, E. S., "Absorption Spectra of Some Diatomic Gases in the Near Infrared," *Astrophys J.*, **50**, 251 (1919).
4. HERZBERG, GERHARD F., "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., 1950.
5. HERZBERG, GERHARD F., "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., 1949.
6. RUARK, A. E. AND UREY, H. C., "Atoms, Molecules, and Quanta," McGraw-Hill, New York, 1929.
7. MULLIKEN, R. S. "Interpretation of Band Spectra," *Rev. Mod. Phys.*, (Parts I, IIa, IIb, **2**, 60, 506 (1930), IIc, **3**, 89 (1931), III, **4**, 1 (1932).
8. DENNISON, D. M., "The Infrared Spectra of Polyatomic Molecules," Part I *Rev. Mod. Phys.*, **3**, 280 (1931), Part II *ibid.*, **12**, 175 (1940).
9. BARNES, R. BOWLING, LIDDEL, UERNER AND WILLIAMS, VAN ZANDT, "Infrared Spectroscopy, Industrial Applications," *Ind. Eng. Chem. (Analytical Ed.)* **15**, 659 (1959).
10. American Petroleum Institute Project 44, Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.
11. Sadtler Research Laboratories, 1517 Vine Street, Philadelphia, 2, Pa.
12. BARNES, R. B. AND GORE, R. C., "Review of Fundamental Developments in Analysis—Infrared Spectroscopy," *Analytical Chemistry*, **21**, 7 (1949).
13. GORE, R. C., *Analytical Chemistry*, **22**, 7 (1950), **23**, 7 (1951), **24**, 8 (1952), **26**, 11 (1954), **28**, 577 (1956), **30**, 570 (1958).
14. BARNES, R. BOWLING, GORE, R. C., STAFFORD, R. W. AND WILLIAMS, V. Z., "Qualitative Organic Analysis and Infrared Spectrometry," *Analytical Chemistry*, **20**, 402 (1948).
15. COLTHUP, N. B., "Spectra-Structure Correlations in the Infrared Region," *J. Opt. Soc. Am.*, **40**, 397 (1950).
16. RANDALL, H. M., FOWLER, R. G., FUSON, NELSON AND DANGL, J. R., "Infrared Determination of Organic Structures," D. Van Nostrand Co., (1949).
17. MEYER, C. F. AND LEVIN, A. A., "Absorption Spectrum of Hydrogen Chloride," *Phys. Rev.*, **34**, 44 (1929).
18. KIESS, C. C., CORLISS, C. H., AND KIESS, H. K., *Program of the National Academy of Sciences*, Washington, D. C., April 1960.

CURTIS J. HUMPHREYS

BETA-RAY SPECTROSCOPY

ELECTRON BACKSCATTERING, ANALYSIS BY

The most recent application of electrons (β -particles) to analysis is the remarkable demonstration at Los Alamos by Dr. and Mrs. Ralph H. Müller^{1, 2} that the backscattering is a discontinuous function of atomic number, but strictly linear in Z within each period of the periodic table, and that the backscattering from compounds can thus be predicted with high precision. The very simple apparatus consists of a collimated source of β -particles from strontium-90 which impinges on the sample, (solid, liquid or solution) after screening to transmit only the 2.18 mev betas from the daughter element yttrium-90; and a mylar window admits the backscattered particles into a methane proportional counter.

A calibration plot of relative backscattering shows that discontinuities or changes in slope appear precisely at atomic numbers 10, 18, 36 and 54 corresponding to rare gas configuration of neon, argon, krypton and xenon. With linear equations over each range, $BS = aZ + b$, where BS is backscattering in per cent, Z is atomic number and a and b are constants, it is possible to calculate the values for remaining elements which are closely in agreement with experimental values. Hydrogen exhibits negative backscattering, so that carbon in hydrocarbons accounts for more backscattering than the compounds, the difference being directly proportional to the hydrogen content. Similarly corrections can be made for hydrates. The difference in backscattering between hydrogen and deuterium has considerable theoretical importance. Measurements have been made very successfully on a number of organic compounds in single and multiple component-systems using the following BS values in per cent: C ($Z = 6$), 5.230; N (7), 6.461; O (8), 7.692; F (9), 8.923; S (16), 15.953; Cl (17), 16.920; Br (35), 29.560; I (53), 36.208. Isomers scatter identically, but halogenated compounds for example, are distinguished with high precision. It is ob-

vious that β -particle backscattering as well as absorption can be used in continuous monitoring of process streams by use of a count-rate meter and recording potentiometer. Highly significant progress in industrial β -ray analysis was reported by research analytical chemists of the Dow Chemical Company³ at the April 1960 meeting of the American Chemical Society. With a 20-millicurie Sr 90-Yt 90 β -ray source and an ionization detector electrometer measuring circuit, differences of only 0.004 per cent in backscattering intensities can be detected—a 10-fold improvement.

Quantitative analysis of impure methyl isopropenylketone gives the same precision as the classical microchemical analysis. The β -ray technique analysis runs less than 30 minutes; the chemical analysis takes over three hours. Hydrogen analyses in binary and ternary compounds and mixtures are especially accurate by β -ray methods. Standard deviation in the experimentally determined weight fraction of hydrogen in 66 compounds and mixtures was only 0.03 per cent, the group reports.

While analysis of hydrocarbons by β -ray absorption or transmission techniques has been carried out and commercial instruments are available for the analysis, β -ray backscattering offers a distinct advantage for this type of analysis. Transmission measurements demand a very accurate mass density determination (± 0.0001 gram/ml). This requires sample thermostating. But β -ray backscattering analysis of binary compounds requires only a density accuracy to ± 0.01 gram/ml—well within the precision of specific gravity hydrometers. Faster and simpler analysis with no sacrifice of precision is the consequence.

The backscattering method is also equally applicable to continuous plant stream analysis, especially for binary materials and two-component streams. For example, it can be used to determine the carbon-hydrogen ratio during the ethylation of benzene.

REFERENCES

1. MÜLLER, D. C., *Anal. Chem.*, **29**, 975 (1957).
2. MÜLLER, R. N., *Anal. Chem.*, **29**, 969 (1957).
3. GRAY, P. R., CLAREY, D. H., AND BEAMER, W. H., reported in *Chem. Eng. News*, Apr. 18, 1960, p. 86.

G. L. CLARK

THEORY, INSTRUMENTATION AND APPLICATIONS

Since the discovery of radioactivity by Becquerel in 1896 a great volume of research work has been devoted to the nature of the radiation spontaneously emitted in the process of the decay of unstable nuclei of the naturally occurring radioisotopes. Subsequently a large number of artificial or "synthetic" radioisotopes, also emitting these rays upon decay, have been produced by the bombardment of stable atoms by electrons, protons, neutrons and other projectiles in reactors, cyclotrons, betatrons and other accelerators. It was demonstrated that the principal types of radiations associated with radioactive disintegrations or decay are α -particles (doubly positively charged He nuclei), β -particles (electrons) and γ -rays (electromagnetic photons).

It is evident then that the analysis particularly of β -ray and γ -ray spectra (q.v.) should reveal invaluable information concerning the nuclei of emitting atoms in terms of structure, energy levels and mechanism of the spontaneous processes of decay. Such indeed has been the case in the development of nuclear spectroscopy. Actually β -ray spectroscopy in its close interrelationship with γ -ray spectroscopy, is a subject of great complexity. This fact can be judged from the masterly and exhaustive 959 page treatise "Beta- and Gamma-Ray Spectroscopy" edited by Kai Siegbahn, the distinguished Swedish physicist.* For β -ray spectroscopy the complications arise (1) from the emission of β -rays from radioactive nuclei as a primary process; (2) from *conversion* processes

in which γ -rays from decaying nuclei or, along with x-rays, from external sources are absorbed by atoms with attendant ejection of so-called photoelectrons from the atomic shells (K, L, M, etc. levels) surrounding the nuclei, thereby permitting analysis of converted γ -ray spectral energies from the energies of the liberated β -rays; (3) and from other intra-atomic mechanisms which result in liberation of *Auger* electrons, photo and Compton secondary electrons, K-capture by the nucleus of an electron in its own K orbital, followed by emission of characteristic x-rays when the vacancy is filled, and others.

Spectroscopy of β - and γ -rays did not begin until 1911, when it was found that β -radiation from radioactive species contained both a continuous component and discrete lines. The existence of long "series" of β -lines, the energy differences of which corresponded to the differences of the atomic shells of the daughter product led to the interpretation that a series of photoelectrons are expelled by monochromatic γ - quanta emitted from the nucleus. More recently, however, it has been theoretically and experimentally proved, according to Siegbahn, that conversion (γ to β energies) must be regarded as an additional mode in which nuclei decay. In other words the excited state of a nucleus can be de-excited either by the emission of a γ -quantum or by a direct interaction with the atomic core in which case a conversion electron from one of the atomic shells is emitted. This conversion phenomenon has been extremely useful in the study of the finer details of radioactive decay, for the energy measurements of β -lines permit calculation of the corresponding energies of nuclear transitions, and the intensities permit determination of the quantum-mechanical properties of different nuclear states. Spin and parity changes in nuclear decay can be evaluated leading to the nuclear shell theory, now well established, complemented with the concept of collective nuclear motion. In complete analogy with optical molecular spectra, there are made possible rotational and vibra-

* Published in Holland, 1955; distributed by Interscience Publishers, N. Y.

BETA-RAY SPECTROSCOPY

tional levels in nuclei. Instead of a static nuclear field there must be a dynamic field acting on a single particle. The "molecular" aspect of nuclear structure derived largely from the facts of β - and γ -ray spectroscopy is one of the most promising contemporary developments.

Since 1934 the continuous β -ray spectrum upon which the sharp lines are superimposed is accounted for by the hypothesis of the neutrino particle, now an experimentally established identity, by means of which it is possible to account for the relation between decay rate and maximum energy of β -particles. It should be remembered that within a nucleus a neutron is supposedly stable but outside, after an average of 18 minutes, it spontaneously ejects a β -ray and turns into a proton. The proton and electron together are 1.5 electron masses lighter than the neutron, and this mass, equivalent to 780,000 electron volts of energy, is lost in the decay. To account for the discrepancy Pauli suggested that another particle with a zero rest mass is formed in the decay and carries the missing energy. Fermi named this the neutrino and constructed a theory that the neutron continuously loses and regains an electron and neutrino by a virtual process which becomes real because the lost mass provides the energy.

Beta-ray Spectrometers

The experimental work in β - and γ -ray spectroscopy can be performed by means of a large number of different instruments, but of all these the β -ray spectrometer is the basic instrument. Combined with suitable particle detectors, magnetic or electric fields of various stages can resolve complex nuclear spectra of particles or photons (as converted or secondarily produced particles). Thus γ -ray spectra (q.v.) can be resolved by diffraction with a crystal analyzer as is common for x-ray spectroscopy (q.v.), especially with efficient pulse height analyzers. But the

resolution is 10% compared with 1–2% for magnetic spectrometers, so that there is this advantage in the conversion electron spectra.

A large number of magnetic and electrostatic spectrometers have been designed to meet various situations, but in general the effort has been to collect as much as possible of the nuclear energy into the spectrometer and to attain the maximum of energy resolutions. As indicated the spectrometers may be classified into magnetic and electrical, depending upon whether a magnetic or an electrostatic field is produced to act upon—bend and focus—the stream of negatively charged electrons. The former type far outnumbers the latter. These are further classified into "flat" spectrometers in which magnetic lines of force are perpendicular to the electron paths and thus focus the beam in a circle in one plane; or "helical" (all types of lens fields) in which the lines of force are parallel with the direction of the electron paths so that the longitudinal field is "space-focusing."

The basic relationships are simply described as follows. An electron (charge e , velocity v) moving in a homogeneous magnetic field B in a plane perpendicular to the lines of force describes a circular path with radius of curvature ρ . The motion is given by the equation

$$Bev = \frac{mv^2}{\rho}$$

where

$$m \text{ (the mass with relativity correction)} = \frac{m_0}{1 - \frac{v^2}{c^2}}$$

The momentum is $p = mv = e \cdot B \rho$. In β -ray spectroscopy the momentum of the electron is expressed by $B \rho$, since this value indicates what magnitude of magnetic field and apparatus dimensions are required to handle electrons in a given experiment. Momentum

of focused electrons, instead of energy, is used because it is proportional to the magnetic field, (or the exciting electric current if iron is used), and not the energy. In electrostatic spectrometers the energy is proportional to deflecting voltage, but $B\rho$ coordinates are still generally accepted. For plotting the momentum or the energy distribution curve from the number of counts P (Geiger, proportional, scintillation), the following relations exist.

	Magnetic		Electrostatic
	$B = \text{constant}$	$B = \text{variable}$	
Values measured			
abscissa	Radius	B	V (voltage)
ordinate	p	B	$\sqrt{v}$
Plotted as momentum distribution curve			
abscissa	p	B	$\sqrt{v}$
ordinate	p	P/B	$P/\sqrt{v}$
Plotted as energy distribution curve			
abscissa	p^2	B^2	V
ordinate	P/p	P/B^2	P/V

Conversion lines with $B\rho = 1000\text{--}3000$ are particularly easy to measure, since 50 keV (kilo-electron volts) representing γ -ray or x-ray energy is equivalent to $B\rho \sim 800$, and 500 keV to $B\rho \sim 3000$. The most accurate relationship expressing energy in keV and momentum in $B\rho$ gauss-cm. is

$$E(\text{keV}) = (510.984 \pm 0.016) \cdot$$

$$(\sqrt{3442.2 \pm 0.2} \cdot 10^{-10} \cdot (B\rho)^2 + 1) - 1.$$

The first determinations of energies of β -particles by their deflection in a magnetic field were made in 1910 by von Baeyer and Hahn. The β -rays from a radioactive wire passed through a narrow slit and, after deviation by the perpendicular magnetic field, were recorded on a photographic plate. This simple device lacking any focusing of the

rays, gave the first evidence of definite lines in the β -ray spectrum. In 1912 Danysz suggested the semi-circular focusing principle which is still of primary importance in β -ray spectroscopy.

Extended details on design, and operation of many modifications of β -ray spectrometers are illustrated in Chapter 3 of the Siegbahn book already referred to. Typical of modern instruments of very high precision is the β -ray spectrum of $\text{Th}(B + C + C^{\text{III}})$, the lines of which are now used for calibration purposes. The strongest lines are as follows:

	$B\rho$ (gauss cm)	Electron Energy (keV)
ThA	534.20 ± 0.06	24.509 ± 0.005
B	652.38 ± 0.07	36.150 ± 0.007
F	1388.44 ± 0.10	148.08 ± 0.02
I	1757.07 ± 0.14	222.22 ± 0.03
Ia	1757.07 ± 0.14	222.90 ± 0.03
J	1811 ± 0.15	234.61 ± 0.03
L	2607.17 ± 0.030	422.84 ± 0.08
X	9986.7 ± 1.5	2526.3 ± 0.5

Scattered and Characteristic Beta Rays

De Broglie was the first to use a simple semicircular β -ray spectrometer to measure the conversion of x-ray to β -ray energy, and thus to provide an independent means of evaluation of electronic energy levels in atoms.

X-rays impinging upon the surface of a secondary radiator eject photoelectrons. If the radiation is monochromatic (frequency ν_0), then the kinetic energy of some of the liberated (scattered) electrons will be $E_k = h\nu_0$ independent of the secondary radiator. The electrons are those so loosely bound in the atoms that the work required for their removal is negligible. In addition, however, other photoelectrons are ejected with kinetic energies that depend upon the particular kind of atom from which they are liberated; hence, their removal has involved a certain amount of work W . If a beam of these electrons is analyzed by causing them to bend in a magnetic field, then all electrons with

the same value of $E_k = h\nu_0 - W$ will register a sharp spectral line on a suitably disposed photographic plate. By means of these characteristic β -ray spectra, De Broglie showed that the energy necessary to eject an electron from an inner atomic shell, which is involved in the correction term W , is simply the quantity of energy representing the energy levels K, L, M, N, etc., which is in turn measured by the frequency values of the critical absorption limits. These β -ray spectra therefore constitute another important method of measuring energy levels. In one photograph for photoelectrons ejected from a silver plate irradiated by the K-radiation of tungsten (and of course producing the secondary fluorescent silver K-radiation), De Broglie obtained six lines, corresponding to six different kinetic energies. He showed that these were:

(1) $h\nu_{\text{AgK}\alpha} - L_{\text{Ag}}$ (where L_{Ag} is the energy required to remove an L electron from the silver atoms, or $h\nu_{\text{AgL}\alpha\beta\gamma}$)

(2) $h\nu_{\text{AgK}\alpha} - M_{\text{Ag}}$

$h\nu_{\text{AgK}\beta} - L_{\text{Ag}}$

(3) $h\nu_{\text{AgK}\beta} - M_{\text{Ag}}$

(4) $h\nu_{\text{WAg}\alpha_2} - K_{\text{Ag}}$

(5) $h\nu_{\text{WAg}\alpha_1} - K_{\text{Ag}}$

(6) $h\nu_{\text{WAg}\beta} - K_{\text{Ag}}$

More recently Robinson and his associates have made notable contributions to the field of magnetic spectra of secondary electrons. By means of greatly improved experimental methods the values of energy levels have been determined for many of the chemical elements, including measurement of absorption limits in the range of long wavelengths in which the crystal-grating method is not practicable. This work has also included measurement of energy levels in multiply ionized atoms. Not only do the magnetic spectra yield energy values of secondary electrons that are ejected from inner levels by action of the primary x-rays; the secondary fluorescent x-rays generated in the radi-

ator are also effective in liberating electrons. The process may be pictured as follows: a K electron is ejected through the agency of the primary x-rays, followed by the transition of an L electron, for example, to fill the vacancy. Normally a $K\alpha$ -ray is emitted as a consequence of liberation of energy. However, this energy so released can be transformed in the atom into forms other than the quantum of radiation (*the Auger effect*). For example, the transition $L \rightarrow K$ (i.e., from the state K with one electron missing, to the state L) may lead to the ejection of an M (Auger) electron with a kinetic energy represented by the difference between the first energy ($L \rightarrow K$) and the work required to remove this M electron from the atom. This work is greater than that which normally corresponds to the M level, for an electron is missing from an inner level with the result that there is diminished screening of the positive nucleus. Therefore the work of separating an outer electron is equal to that required normally for the element of next higher atomic number. Such processes have been experimentally verified in Robinson's work.

Chemical Analysis by the Photoelectron Spectrometer

Only recently has the photoelectron spectrometer come into use for chemical analysis with the perfection of ultrathin-windowed Geiger counters for detection. An instrument for this purpose, together with typical photoelectron spectra for copper, zinc, silver, gold, and binary alloys, is described by Steinhart and Serfass.¹ From the spectrum of an 80 atomic per cent Ag-20 atomic per cent Au, these authors have obtained a fairly good quantitative analysis. The equation used is $T = h\nu_0 - h\nu - w_0$, where ν_0 = frequency of primary, or exciting, radiation, ν = frequency of fluorescent radiation (instead of characteristic absorption), and w_0 = work

function of irradiated sample. Thus the major Ag peak is identified as $\text{MoK}\alpha\text{-AgL}\beta$, and others as $\text{MoK}\alpha\text{-AgL}\beta$ and $\text{MoK}\alpha\text{-AuM}$.

1. STEINHARDT, R. G. AND SERFASS, E. J., *Anal. Chem.*, **23**, 1585 (1951); **25**, 697 (1953).

G. L. CLARK

DIFFERENTIAL THERMAL ANALYSIS

Study of thermal reactions can be made easier and the interpretation of results clearer by using differential thermal analysis as a correlative technique. The technique can be used to determine the temperatures of reaction or transformation and thus establish the limits required for other studies.

Differential thermal analysis is a technique by which phase changes are detected as a sample is heated or cooled through the transition temperature. The change may be in state, e.g., melting, vaporization or crystallographic phase transition, or chemical, e.g., decomposition, combustion, or chemical reaction. The technique may be used for qualitative and, to a limited degree, quantitative analysis. It is also useful for establishing phase diagrams and is a valuable tool in forensic chemistry. The method is specific for compounds, rather than for ions or elements.

The method is widely used in the earth sciences; chemistry, metallurgy and ceramics. The examples given below are typical but not all-inclusive. (1) The chemical applications of differential thermal analysis are varied. Phase diagrams of soaps, phosphors and salt systems have been obtained. The method is used for testing raw materials, for process control and to differentiate organic isomers or similar materials such as starches. It has recently been used to determine the activity of catalysts by measuring the heat effect due to chemisorption of a catalyst poison gas. (2) Phase transitions in metals and alloys are of great interest to metallur-

gists. Differential thermal analysis as well as calorimetry is being used in this field. (3) Ceramists use differential thermal analysis to study minerals and mixtures for raw materials and to determine the effect of firing processes. The method has also been used to study synthetic raw materials for ceramic production.

Historically, differential thermal analysis is derived from the work of Le Chatelier and Saladin in calorimetry. Roberts-Austen and Burgess introduced the true differential technique. The method was used first in metallurgy but later gained wide use in clay mineralogy and, more recently, in chemistry and other fields.

In general, the sample and a reference material are heated or cooled in close proximity and the difference in temperature between them measured or, usually, recorded. This temperature difference, ΔT , may be plotted directly as a function of the furnace, reference, or sample temperature, or as a function of time which is then related to these. The reference material is one which undergoes no phase change in the temperature region being studied. The most common material is calcined aluminum oxide.

The specimen and reference materials are usually placed in separate holes in a sample block. One junction of a differential thermocouple is placed in the center of each and the assembly is placed in a furnace. The furnace is then heated at a constant rate through the temperature region of interest.

So long as no phase changes occur the

DIFFERENTIAL THERMAL ANALYSIS

specimen and reference are heated at very nearly the same rate and the temperature difference is very small. When, say, an endothermic change occurs, the specimen temperature lags behind the reference temperature because of the heat required to carry out the transition. When the transition is complete, thermal diffusion brings the sample back to equilibrium quickly. The resulting plot of ΔT vs. T would show, in a conventional thermogram, a smooth trace with a ΔT of near zero followed by a more or less sharp depression and a subsequent return to near zero. An exothermic transition would cause an increase in temperature of the specimen because of the heat supplied by the reaction. The shape of the peak or depression and the temperature at which it occurs are qualitative aids to identification of the reacting species.

The equipment must be designed carefully. The furnace must have a uniform temperature zone large enough to enclose the sample block to be certain that the temperature gradients at the specimen and reference holes will be the same. The furnaces are usually movable, so that the specimen and reference materials may be mounted on a stationary support and the furnace moved horizontally or vertically to surround the sample holder.

For a base metal alloy-wound furnace, a motor-driven variable autotransformer will give a nearly constant heating rate. For platinum-wound furnaces a programming device is required because of the great change of resistance with temperature of the platinum or platinum alloy. This control device could be, for example, a cam-driven variable autotransformer. With either type of furnace more elaborate controls may be used to change the input voltage as needed to keep the furnace heating at the desired rate. For example, if a strip chart recording potentiometer with a linear temperature scale is used, a second slidewire (linear) may be put on the slidewire shaft. Then, using a motor-

driven linear slidewire supplied with the same voltage, the signals from the two moving contacts may be compared electronically and any difference between them used to advance or back off a variable autotransformer. As the motor-driven slidewire advances steadily, the autotransformer is adjusted to supply the proper amount of power to advance the temperature at a constant rate.

The recording devices may be electrical or optical, or a combination. The strip chart recorders, whether electrically or optically operated, are simpler experimentally than photographic recording and the record can be seen during the experiment. The temperature and temperature difference may be recorded on separate recorders but, more recently, X, Y-recorders have been used to plot ΔT vs. T directly and two pen instruments record T and ΔT simultaneously. The X, Y, system provides a simple record; the X_1 , X_2 , system will show any errors in the heating cycle. Multipen recorders have been used to record a number of thermograms simultaneously.

Opinions on the best type of sample holder are less than unanimous. Metal blocks provide a heat sink which will reduce the magnitude of the difference signal but they give low temperature gradients in the vicinity of the sample and consequently, more uniform heating. Ceramic blocks, because of their lower thermal conductivity, give sharper difference signals but higher gradients. Small crucibles are also used. They do provide a smaller heat sink, but lack of symmetry with respect to the furnace walls will give unequal heating. Further, very thin walls—even in metal crucibles—will permit sufficient temperature differences in various parts of the surface to diminish the height and increase the width of the peak or depression. Metal crucibles of sufficient wall thickness, properly placed, give very sharp phase change indications. In any case, a sample holder must be chosen which will not react with the specimen or reference.

The thermocouples may be chromel-alumel for temperatures up to 1000°C or platinum-rhodium or platinum or another noble metal or alloy for higher temperatures. Platinum—10 % rhodium vs. palladium—40 % gold gives as high sensitivity as chromel-alumel and can be used to near 1500°C.

Minor variables must be controlled if a number of thermograms are to be compared. The particle size, packing and the size of the thermocouple bead, for example, are not usually critical. In quantitative determinations, however, they must be kept nearly constant, since the peak height or area will be measured. For some types of samples, of course, the atmosphere must be controlled. Alternatively, the atmosphere may be controlled in order to learn the nature of a reaction, e.g., decomposition of a carbonate will occur at some higher temperature in an atmosphere of carbon dioxide.

Differential thermal analysis is being used to a rather limited degree in the study of high temperature reactions. The information obtained can be correlated with that obtained by other high temperature techniques—x-ray diffraction, thermogravimetric and optical analysis, and electrical conductivity measurements.

Recent advances in furnace design permit the trapping—or immediate analysis—of gaseous reaction products. The furnace atmosphere passes through the sample and out of the furnace so that the atmosphere and products may be conducted into traps, a gas chromatograph, or a gas density or thermal conductivity detector. Combinations of these, with separate recording facilities, have been used to determine uniquely—and immediately—the nature of the decomposition indicated by the differential thermal analysis apparatus.

As a correlative technique with high temperature diffraction techniques, differential thermal analysis is used to select temperatures at which to study the material. Obviously, the regions above and below each

phase transformation or reaction would be studied. Since these are located quite accurately, unnecessary experiments can be avoided. In addition, the thermogram may yield useful information about the kind of reaction or transformation taking place. An exothermic indication obviously shows that the process is irreversible. A wide peak or depression indicates that the process is slow. The area of the deflection gives a measure of the heat involved.

Similarly, for room temperature diffraction studies of high temperature reactions or transitions, differential thermal analysis will show the temperatures to which samples should be heated. Again, it will indicate whether or not the process is reversible. If an exothermic indication is obtained during the cooling cycle, the process is reversible. In this case, the high temperature phase can often be obtained at room temperature by quenching the sample, e.g., in liquid nitrogen, from a temperature above the transition. Here again, differential thermal analysis is useful to determine how well the sample was quenched. The high temperature form, being unstable, will revert to the low temperature form at some temperature below the transition point. This is, of course, an exothermic reaction. If the high temperature form reverts to the low temperature form at a temperature not far below the transition point or if the heat capacities of the two forms are not greatly different, a well-quenched sample will have an area under the peak of about the same magnitude at the area above the depression at the transition point.

For qualitative identification in spectrophotometric studies, differential thermal analysis can be of aid as a rapid and convenient method for obtaining melting and boiling points as well as crystallographic transitions.

Phase diagrams may be obtained quite readily by obtaining thermograms of the end members and, for a simple binary system,

ELECTRON PARAMAGNETIC RESONANCE SPECTROMETRY

four to five mixtures. The mixtures are fused, cooled and ground to assure homogeneity or intimacy of mixing and the thermogram is obtained.

Some attempts have been made to treat differential thermal analysis data mathematically. The treatment requires much independent data. Nevertheless, approximate values of heats of reaction, combustion and vaporization can be obtained readily by straightforward calibration techniques. Quantitative analysis is normally done by

calibration techniques rather than by calculation using any thermodynamic quantities.

A discussion of the theory and practice of differential thermal analysis is given by Smothers and Chiang (Smothers, W. J., and Chiang, Y., "Differential Thermal Analysis" Chemical Publishing Co., Inc., New York, 1958.) This book includes a bibliography as well as a list of nearly three hundred laboratories having differential thermal analysis equipment.

PAUL D. GARN

ELECTRON PARAMAGNETIC RESONANCE SPECTROMETRY

BASIC THEORY AND INSTRUMENTATION

The electron, like the proton (see Nuclear Magnetic Resonance) is a charged particle; it spins and hence has a magnetic field. But it spins much faster than protons (or other nuclei) and so has a much stronger magnetic field than they. The electron has magnetic resonance, discovered by a Soviet physicist, E. K. Zavoisky, in 1944 before Purcell and Block announced nuclear magnetic resonance in 1946; but being a stronger magnet and much lighter than a proton, it precesses much more rapidly in a given magnetic field. Whereas the proton is probed with radio waves in the range of a few megacycles per second, for electrons the frequencies employed are in the microwave range, around 10,000 megacycles per second. Thus when microwaves travel down a rectangular waveguide they produce a rotating magnetic field at any fixed point, which can serve to flip over electron magnets in matter, just as a rotating field in a coil flips protons.

The experimenter may place the sample on a side wall of the waveguide, turn on the microwave radiation and apply an external magnetic field to make the electrons precess.

When the precession rate reaches the resonance value and the electrons flip, they extract energy from the microwaves and the reading on a receiver at the end of the tube dips accordingly.

A simplified block diagram is given in Fig. 1. If the electron has not only an intrinsic magnetic moment along its own spin axis but also one associated with its circulation in an atomic orbit, the electron will possess a total magnetic moment equal to the vector sum of these magnetic moments. The ratio of the total magnetic moment to the spin value is a constant for a given atom in a given environment, and is called the gyromagnetic ratio or spectroscopic splitting factor for that particular electron. The fact that these ratios differ for various atoms and environments and the fact that local magnetic fields depend on the structure of matter permit the *spectral separation* and EPR spectroscopy, a companion to NMR spectroscopy.

Not all atoms and molecules are susceptible to this technique, for in substances in which electrons are all paired the electrons' magnetism is neutralized. But for unpaired electrons—or where there must be a resultant

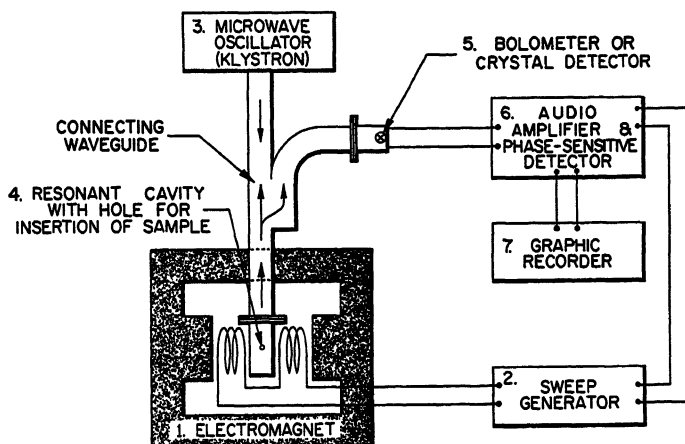


FIG. 1. Block diagram of electron paramagnetic resonance spectrometer.

1. An electromagnet in which the homogeneous gap field H can be swept continuously from near zero to over 5,000 gauss,
2. A sweep generator for producing a small modulation of the main field H at the center of the air gap.
3. A stable microwave oscillator (for example, a klystron) supplying R-F energy at a frequency of 10,000 megacycles per second to
4. A sample cavity resonating at the klystron frequency.
5. A bolometer or crystal detector for demodulating the microwave power reflected from the sample cavity.
6. An audio amplifier, and a phase-sensitive detector for conversion of the detected audio signals into low-noise d.c. signals for display on
7. A graphic recorder.

electronic magnetic moment—electron resonance can be observed. Such effects then may be observed for electrons in unfilled conduction bands, transition element (Mn, Fe, Co, Ni, etc.) ions, odd molecules, free radicals, biradicals, color centers, radiation damage sites, impurities in semiconductors such as barium titanate, and triplet electronic states. As might be expected, applications in the field of biology are particularly fruitful. These are discussed in the following article, together with a pertinent bibliography.

G. L. CLARK

BIOLOGICAL APPLICATIONS

For an introduction to the techniques of Electron Paramagnetic Resonance (EPR) Spectroscopy, the author recommends the book by E. R. Andrew¹ on nuclear magnetic resonance and two review articles: one by J. Wertz² written for the chemist and one by

G. E. Pake³ written for the physicist. These are both excellent articles and together give a complete coverage of the field. In addition to these, the series of articles and examples appearing in the Technical Information Bulletins⁴ of Varian Associates, particularly those in Volume 2 which are written more for the laymen, are strongly recommended.

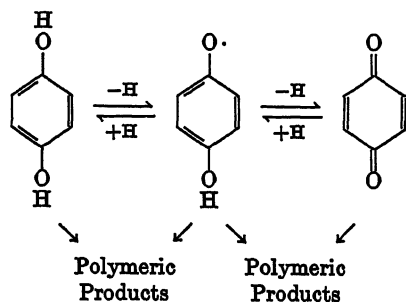
Unfortunately not all atoms and molecules of interest are susceptible to study by this new technique. They must exhibit a resultant electronic magnetic moment. Of these, there are four classes of compounds that are of particular biological interest: (a) odd molecules and free radicals, (b) biradicals, (c) triplet electronic states, and (d) transition element ions. The first three classes might well be expected to occur biologically in (a) univalent redox reactions, (b) enzymatic oxidations (dehydrogenations) and (c) carcinogenesis.

For the past quarter of a century, the idea

ELECTRON PARAMAGNETIC RESONANCE SPECTROMETRY

TABLE I

<i>p</i> -benzoquinone	homogentrisic acid	phenanthrene quinone
<i>o</i> -benzoquinone	polyporic acid	phenolphthal- ein
catechol	tocopherol	ascorbic acid
pyrogallol	1,5-naphthalenediol	nicotinic acid
gallic acid	1,4-naphthoquinone	<i>p</i> -phenylenediamine
quaiacol	1,2-naphthoquinone	<i>p</i> -aminolphenol
arsinol	juglone	benzidine
resorcinol	menedione	diacetyl (see VA EPR at Work #13)
4-ethyl resorcinol	vitamin K ₁	benzil
4-propyl resorcinol	vitamin E	ninhydrin
4-butyl resorcinol	phthiocol	riboflavin
4-amyl resorcinol	anthraquinone	FMN
4-hexyl resorcinol	anthraquinone β-sulfonic acid	indigo
2-nitro resorcinol	alizarin	adrenaline
gentrisic acid	carminic acid	DOPA



has been current that free radicals may participate in biological processes. As far back as 1931, Haber and Willstatter⁵ proposed that a great majority of enzymatic dehydrogenations involved free radical intermediates. In reviewing the history of this one-electron transfer hypothesis in biological oxidations, it is of interest to note that most of the reactants in the metabolic redox systems are even molecules, that is, all electrons occur in pairs. It certainly is within reason to expect then that all electron transfers among these molecules would occur in pairs; however, there exist several instances where the chain of electron transport has as one of its links

a substance, such as cytochrome, which can transfer but one electron under oxidation or reduction. These substances are the metallo-organics. Clearly then, there must exist certain molecules which proceed in their two electron transfer by one-electron steps. It is at this juncture in biochemistry that Michaelis made his now famous proposal "that all oxidations of organic molecules, although they are bivalent, proceed in two successive univalent steps, the intermediate state being a free radical."⁶ Perhaps for the sake of rigor one should understand the term "odd molecule" here, rather than "free radical," but in either event the implication is clear.

The validity of this proposal is subject to experiment, and it is to Michaelis' credit that he supported it experimentally as well as he did. Unfortunately, until the advent of electron paramagnetic resonance, the only recourse was to static susceptibility measurements which at their best could detect no less than 10^{-6} moles. (Recently Brill at the University of Pennsylvania perfected a static balance capable of detecting 10^{-7} molar solutions of paramagnetic molecules.) Whereas some occasional studies, such as those of Pauling, Coryell, *et al.*⁸ on the magnetic susceptibility of hemoglobin, have been of great value, little has been accomplished in checking Michaelis' assumption due to this low sensitivity. E-P-R has aided by increased sensitivity in many cases, and has made a much greater contribution by distinguishing among paramagnetic ions, odd molecules and free radicals.

Much work has been performed with E-P-R on the non-enzymatic oxidation reductions of the simpler biologically occurring quinone and quinoid compounds,⁹ and it may be concluded that these compounds pass through two successive one-electron transfer processes on their way to the final state. Furthermore the lifetime of the paramagnetic semiquinone radical is dependent upon the isomeric form in agreement with observed differences in the oxidation potentials,

and also upon the pH of the solution (the free radical produced by dehydrogenation of the hydroxyl group is stabilized in alkaline solution, while that from dehydrogenation of the amino group is stabilized in acid solution). A partial list of the compounds yielding observable free radical concentrations is given in Table 1.

At this point, the question of polymerization arises. If the lifetime of the free radical intermediate is sufficiently short, the probability of a given polymeric reaction is quite small. This can be seen by studying the parabenzoquinone redox reaction shown in Figure 1. At pH 7 no polymeric side product is detectable but at pH 8 a color change belies these side reactions and at pH 9 a dark brown precipitate appears which is very similar to the melanin pigments. It is to be noted that it is in this pH range that the quinhydrone electrode ceases to be useful.

The control of such free radical reactions by a biological system may thus be performed by both pH and antioxidants. The role of antioxidants is a subject in itself, and their activity in biological systems is of even more interest because of the problem of radiation damage. The antithesis of this effect is produced by radiosensitizers which are good oxidants; e.g., O_2 , quinones, et cetera. Furthermore, those organics that form active free radicals upon reduction are particularly good as sensitizers, suggesting the role of free radicals in radiation damage. The experiments to verify this latter role are few; however, considerable effort is currently being devoted toward this end, and the results will be of great interest. At the present the author is aware of only one experiment which demonstrates free radical production as a secondary process in radiation damage: $10^{-5}M$ riboflavin was reduced by ethyl alcohol radicals formed by reaction with OH and H radicals produced by 650 kv X-rays on the water, 3% alcohol, riboflavin mixture. Experiments such as those reported by Gordy *et al.*,¹⁰ if carried to a proper conclusion, may

offer support here also. In regard to antioxidants, one notes that they often operate by forming dimers, thus reducing the free radical concentration by two with each dimer; e.g., cysteine (a sulfhydryl) going to cystine (a disulfide). An excellent monitor of antioxidant level may be obtained by titrating against a standard free radical solution and using E-P-R as a detector. Blois¹¹ has had excellent success using optical absorption of such solutions as a quantitative measure of reduced free radical and hence antioxidant concentration. It is interesting to note that such measures may prove to be unique radiation dosage monitors. More research needs to be done on the clinical applications of E-P-R than is being done at the present time.

The sensitivity of E-P-R makes possible the observation of free radical intermediates *in vivo*. This has far-reaching implications; however, experiment is slow, largely due to the need for technological developments along the way. Toward this end the first experiments were those of Commoner *et al.*¹² with lyophilized samples. Signals were obtained for a great variety of samples including yeast, blood, rabbit organs, germinated digitalis seeds and barley leaves. As is often the case with preliminary work, many of the signals were false in the sense that they were due to paramagnetic ions or physical damage due to freeze drying and not to metabolically active free radicals.¹³ Nevertheless, the simple fact that signals were observed was sufficient to stimulate further effort, and some beautiful results have been forthcoming. Before discussing these, it is perhaps well to give an example of the possible damage that can result from freeze drying. The spectrum recorded from whole human blood is reproduced in the Varian Associates', (Palo Alto, California) "E-P-R At Work," #9 of a Series; this reveals the partial conversion of hemoglobin to methemoglobin and the physical damage to both molecules by the lyophilization. In addition one records a free

radical signal apparently associated with the snapping open of the porphyrin ring structures of the hemoglobins.

One of the most intriguing biochemical processes is that of photosynthesis—the conversion of photo-energy to chemical energy. Since this process clearly involves oxidation-reduction steps, it is possible that E-P-R may help answer some of the questions. The question of greatest concern is whether the initial molecule is an excited one or a free radical or an ionized species and whether the process is a single or multiple quantum one. Calvin and Sogo¹⁴ and Commoner *et al.*¹⁵ made preliminary E-P-R studies on the chlorophyll system. Light sensitive signals were observed. In attempts to identify the source of the E-P-R signal, Sogo, Pon and Calvin¹⁶ and Tollin and Calvin¹⁷ have reported some excellent work. They have shown by kinetic studies under various conditions of sample preparation and temperature, that the initial specie responsible for the magnetic resonance is not likely to be either a triplet state of chlorophyll or a free radical intermediate in the following chain of enzyme reactions. It is most likely a trapped electron residing on the chlorophyll molecule which renders this molecule a semiconductor of sorts. This is consistent with previous assertions by Bradley and Calvin¹⁸ and independently by Katz that a semiconductor state is probable. More work of this quality is needed.

One may review also the progress made in examining enzymatic oxidation-reduction reactions. Again free radicals have been observed, first by Beinert¹⁹ and then by Commoner *et al.*¹⁵ and Ehrenberg and Ludwig.²⁰ However, as shown by Beinert, the kinetic studies indicate that the observed signals are not associated with the primary enzyme-substrate reaction and may offer only secondary information. Much careful work is required here to clarify the situation.

The whole problem of carcinogenesis is still open for study. In an attempt to corre-

late the action of such a variety of carcinogenic agents as sodium hydroxide, UV and ionizing radiations and thousands of organic compounds, a free radical intermediate always suggests itself. Smog studies and recent work by Lyons *et al.*²¹ point up the high active radical content of soot and tobacco smoke and their possible connections with lung cancer.

In summary one may say that free radicals have been implicated in (a) biological oxidation-reduction reactions, (b) radiation damage and photosynthesis, (c) carcinogenesis.

Electron paramagnetic resonance has brought sufficient sensitivity and discrimination to observe free radical intermediates *in vivo*; however, present results are of a preliminary nature and the validity of certain published conclusions is subject to more careful study. Much work remains, and E-P-R will serve as a unique and powerful tool in such investigations.

REFERENCES

1. ANDREW, E. R., "Nuclear Magnetic Resonance," Cambridge University Press.
2. WERTZ, J. E., *Chem. Rev.*, **55**, 829 (June 1955).
3. PAKE, G. E., Volume II, Chap. I of "Advances in Solid State Physics," edited by F. Seitz, Academic Press (1956).
4. Technical Information Bulletin, Vol. 1 and 2, Varian Associates, 611 Hansen Way, Palo Alto, California.
5. HABER, F. AND WILLSTATER, R., *Ber. Deut. Chem. Gesell.*, **64B**, 2844 (1931).
6. MICHAELIS, L., in "Currents in Biochemical Research," S. E. Green, Ed. (Interscience, New York, 1946).
7. BRILL, A. S., DERHARTOG, H. AND LEGALLAIS, V., *RSI*, **29**, 383 (1958).
8. PAULING, L. AND CORYELL, C. D., "The Magnetic Properties and Structure of the Hemochromogens and Related Substances", *Proc. Nat. Acad. Sci.*, **22**, 159-210 (March 1936).
9. BLOIS, JR., M. S. AND SANDS, R. H., "Free Radicals and Biological Systems", Proceedings First Annual Conference of the Biophysical Society, Columbus, Ohio (1957). ADAMS, M. A., BLOIS, JR., M. S. AND SANDS, R. H., *J. Chem. Phys.*, **28**, 1774 (1958).

10. GORDY, W., ARD, W. B. AND SHIELDS, H. "Microwave Spectroscopy of Biological Substances", *Proc. Nat. Acad. Sci.*, **41**, 983-996 (November 1955).
11. BLOIS, JR., M. S., *Nature*, **181**, 1199 (April 26, 1958).
12. COMMONER, B., TOWNSEND, J. AND PAKE, G. E., "Free Radicals in Biological Materials", *Nature*, **174**, 689 (October 9, 1954).
13. SANDS, R. H., WEAVER, H. E. AND FRANKEN, P. A., "Paramagnetic Ions in Blood Sera", Proceedings First Annual Conference of the Biophysical Society, Columbus, Ohio (1958).
14. CALVIN, M. AND SOGO, R. B., "Primary Quantum Conversion Process in Photosynthesis", Electron Spin Resonance, *Science*, **125**, 499 (March 15, 1957).
15. COMMONER, B., *et al.*, "Biological Activity of Free Radicals", *Science*, **126**, 57 (July 12, 1957).
16. SOGO, P. B., PON, N. G. AND CALVIN, M., *Proc. Nat. Acad. Sci.*, **43**, 387 (1957).
17. TOLLIN, G. AND CALVIN, M., *Proc. Nat. Acad. Sci.*, **43**, 895 (1957).
18. BRADLEY, D. F. AND CALVIN, M., *Proc. Nat. Acad. Sci.*, **41**, 8, 563 (1955).
19. BEINERT, H., to be published.
20. EHRENBERG, A. AND LUDWIG, G. D., *Science*, **127**, 1177 (May 16, 1958).
21. LYONS, M. J., GIBSON, J. F. AND INGRAM, D. J. E., *Nature*, **181**, 1003 (April 5, 1958).

R. H. SAND

EMISSION SPECTROSCOPY—LIGHT

ACCURACY IN SPECTROCHEMICAL ANALYSIS*

Abstract. Accuracy is one of the broad areas of spectrochemical analysis where improvement by an order of magnitude would result in vast new fields of application. This article discusses the subject under the topics of sampling, the source, electrodes, the spectrograph, photometry and calculations. New techniques for reducing variables will be discussed. These include optics for reducing the effects of arc wandering, the Elpac for reproducible mechanical packing of powders into electrodes, devices for mechanically traversing a flat sample during sparking, the Stallwood jet and the enclosed arc chamber for controlled atmosphere excitation of samples.

Introduction. Many potential applications of spectrographic analysis lie dormant simply because present day accuracy is not good enough. Not only is this true in industry where improved accuracy would mean superior quality control as well as savings in money, but in biology and medi-

cine better accuracy could result in a new diagnostic tool to tell the researcher why nature goes wrong.

Sampling. The scapegoat of all analytical techniques is sampling. After a sample is consumed, no one can argue that it once truly represented the average composition of the material being analyzed. The reader is referred to an excellent treatise on the subject (Ref. 1, p. 51) which discusses the reduction of a production batch to a laboratory size sample. The spectrographic problem really begins at this point, however, because the spectrograph "sees" only a few milligrams of the actual sample and any segregation whatsoever is greatly magnified.

One method of trimming segregation effects in point-to-plane techniques is that of taking multiple, superimposed exposures at different places along the sample. Another, and one that is readily automated, is to move the sample slowly and uniformly during the sparking. Hurwitz^{2, 3} showed how traversing segregates aids in obtaining a true determination and, further, that certain elements, which ordinarily spark off at the

* Abridged version of article in *Applied Spectroscopy*, **13**, 85 (1959). By permission.

EMISSION SPECTROSCOPY—LIGHT

TABLE 1. SPECTROCHEMICAL ANALYSIS OF CAST IRON
Deviation from Wet Chemical Values, %

Element	Single Determination	Sweep Method	Four Superimposed Spectra
Mo	5	3	2
Cr	6	3	2
Ni	4	2	1
Mn	5	4	3
Si	13	4	5

beginning of the exposure, have a constant intensity with time when new areas of the sample are continuously being sparked. He cited⁴ Al and Mg determinations in zinc-base alloys. Ordinarily, spectral line intensity of these elements drops sharply after the first few seconds, but by using a moving specimen, the sparking-off effect is removed. Improved results were confirmed in the analysis of cast irons by Clark⁵ who moved the sample linearly during the sparking so that the sparked area was equivalent to eight stationary burnings. As shown in Table 1, the technique aids markedly in matching spectrographic with wet chemical determinations.

Similar results with the moving sample technique were also observed by Eckhard and Koch.¹⁹ Using a high voltage a.c. arc source they found that moving the sample increased the reproducibility of the analysis and at the same time enhanced sensitivity to certain trace elements in steel.

To take advantage of the sweep technique, a Petrey Stand with a slowly rotating table is manufactured by Spex Industries. The speed of traverse is determined by the choice of motor but about 90° per 30 seconds—the normal sparking time—is suggested.

For powders the sampling problem has a number of aspects often overlooked: particle size differences, adsorption and absorption of water vapor and atmospheric gases, packing of the powder into the electrode, to name a few. Recognizing these problems,

Tingle and Matocha,⁶ converted a method normally considered but semi-quantitative into one with quantitative accuracy. Their technique involves fusion of samples with lithium borate serving to homogenize the sample and convert it to a common matrix simultaneously. The sample thus treated is ground and screened so that only a selectively chosen particle range is used in the analysis.

Feldman²⁰ has recommended fusion with ammonium bisulfate to accomplish the same purpose. This reagent possesses the additional advantage for trace analysis that the excess reagent can be removed by evaporation on a hot plate at a relatively low temperature.

Packing electrodes is a problem neatly handled with the Elpac, a new machine which automatically tamps craters full. An excess of the material is placed in a disposable polyethylene funnel perched snugly around the neck of the electrode. A tamper is lowered into position and a fixed vibration packs the crater in a few seconds.

Both uniformity and tight packing are achieved with the instrument. In three out of four typical samples, the amount of material packed is reproduced within around 1 %. Furthermore, the amount packed averages around 50 % more than that obtained by hand packing.

The Source. Spark sources have been improved steadily in recent years. The use of an air blast at the auxiliary gap helps stabilize the spark. Controls of the auxiliary gap spacing and osciloscopic observation of rate of discharge of the spark are helpful in reducing variables. Superior materials and shapes of the auxiliary gap electrodes also aid in maintaining spark stability. While too new to evaluate, the Bardocz electronically controlled spark⁸ appears promising.

Feldman and Ellenburg have formulated a procedure⁹ by which, they claim, optimum reproducibility is obtained from their spark source:

1) Auxiliary gap opened to 10 mm or wider.

2) Autotransformer in primary circuit set at zero.

3) Source turned on.

4) Autotransformer adjusted to give a predetermined voltage across its variable arm.

5) Auxiliary gap narrowed until one breakdown occurred on each half cycle.

6) Autotransformer adjusted to give the desired number of breaks per half cycle.

Variables such as cleanliness, smoothness, and shape of the auxiliary electrodes, as well as resistivity of the ambient atmosphere which is temperature and humidity dependent, are avoided by using this procedure. In the opinion of the authors, it aids in reproducing the curve of current *vs.* time from one discharge to the next.

Attempts have been made to couple the advantages of the spark's stability with the arc's sensitivity and such hybrid sources may now be obtained commercially. In pure arcs—still the sources of highest sensitivity—several new developments are notable. The constant current dc arc is one. Through electronic control, the dc arc may be maintained within a few percent. Since the drift of an arc as the sample is consumed and the gap widens may amount to 100 %, a constant current dc arc should result in superior overall accuracy. A commercial source is not yet available in the U. S. A., but three spectrographers have independently built such units. They are L. E. Owen¹⁰ of Goodyear Atomic Corporation, E. Ziemendorf (unpublished) of the Carborundum Company in Niagara Falls and D. O. Landon (unpublished) of Spex Industries. Incidentally, a bonus gotten with the constant current dc arc is potentiometer control of the current instead of the cumbersome motor-driven heavy iron core reactor. The pot permits accurate settings before a run is made and rapid changes in current without overshooting.

The a.c. arc, although convenient to use in

point-to-plane technique, is known to give poor reproducibility with some electrode materials owing to the persistence of a glow discharge for an appreciable (but uncontrollable) fraction of every half cycle. This difficulty is largely prevented by use of a spark-triggered or thyatron-triggered a.c. arc source.

Over the years, there have been many attempts to tame the dc arc through the use of external contrivances. Magnets have been used both to constrain the arc column and to rotate it at fixed speed. Gas jets, double arcs, center-post electrodes are still other innovations aimed at tranquilizing the easily excitable arc.

In the Stallwood jet¹¹ now used in dozens of laboratories, an annular curtain of gas is blown upwards around the arc column to restrain arc wander. Compressed air may be used but, to achieve the added benefit of increased sensitivity and suppression of cyanogen bands, mixtures of argon and oxygen (30 to 50 % of the latter) are recommended.

Improvement in accuracy through the use of the Stallwood jet has been confirmed by a number of spectrographers since the original article was written in 1954. Joensuu,¹² describing its use in the analysis of rare earths on a routine basis, cites the additional advantage that fumes are blown out continuously so there is less self-absorption. The spectrograms dramatically illustrate the improvement in line-to-background ratio especially in the region of the CN bands.

Other major advantages of the Stallwood jet are reduction of matrix effects and prevention of selective volatilization of low boiling elements. This is accomplished through the use of deep crater electrodes in which successive layers of sample are burned away while lower layers remain cool. The electrode is placed so that it protrudes by 1-2 mm above the jet housing. As it is consumed in the arc, a rod is used to push it upwards through the hollow stud.

Inert gas atmospheres have been the subject of numerous papers and the general opinion seems to be that decided improvement in accuracy and sensitivity may often be achieved. The reader is referred to the article by Thiers and Vallee¹³ for detailed information. A recent article by Hammaker and associates¹⁴ illustrated the advantages of using an atmosphere of argon-oxygen in suppressing the cyanogen band intensities. From the viewpoint of accuracy, the result is to remove background almost completely from behind many sensitive spectral lines and so permit their use without having to make inaccurate background corrections.

Fry and Schreiber demonstrated how analytical accuracy could be improved when miscellaneous samples of steel are run by the use of an air blast¹⁵ directed at the spark gap. Variations in chemical composition, physical size and shape, and metallurgical history affect the analytical curves less when an air blast is used.

Electrodes. An unpublished report by S. R. Wiley illustrated how precision could be materially improved step-wise by going from $\frac{1}{4}$ " to $\frac{3}{16}$ " to $\frac{1}{8}$ " diameter electrodes. With his Wadsworth Spectrograph cylindrical optics were used so that the arc column was focused at the slit in the horizontal plane. Accordingly, wandering of the arc off axis caused large changes in the intensity of the slit. By restricting the wander with a narrow electrode, this effect was strikingly reduced.

While discussing electrodes, the subject of physical properties of graphite should be considered. Taking the electrode for granted, the spectrographer does not often question their uniformity from one to the next. Yet W. R. Kennedy,¹⁶ discovered some surprising differences. Using eight types of graphite rods of American and foreign manufacture, he sparked the same sample of cast iron nine times with each rod, machining it after every exposure to a hemispherical tip of 30°. Coefficient of variation for Si and Mn determi-

nations varied from 1.50 to 3.90 %, and from 1.54 to 3.02 % respectively.

The shape of an electrode is, as can be judged from the tremendous number of preforms now available, meaningful in attaining high accuracy. Selective volatilization is, for example, very directly related to accuracy. If one were running a sample for magnesium and tungsten in a conventional undercut electrode, magnesium would volatilize out during the first few seconds of arcing, tungsten during the last few. Using such electrodes, the determinations of these elements is thus subject to inherent errors. In addition, refractory elements often wind up as beads which drop out of the cup before they are completely consumed. For the determination of many elements of varying volatilization rates, Landon¹⁷ found that a very deep ($\frac{1}{2}$ ") crater in a narrow thin-walled electrode produced similar burn-off curves for many elements of varying volatility. As already mentioned, Stallwood¹¹ used deep, narrow electrodes with his jet to reduce selective volatilization and, consequently, matrix effects.

An interesting new shape capable of holding an oxide bead until it is burnt to completion has been described by Slavin.²¹ His modification is obtained from a conventional cup electrode by drilling a sharp conical hole in the center of the cup, into which the oxide bead recedes as the walls of the electrode burn down.

Weather. Spectrographers, too, are bothered by weather's unpredictability, as witnessed by the fact that so many laboratories are air-conditioned. In practice, however, while it is well known that temperature, pressure and humidity variations are factors influencing spectrochemical results, air-conditioning usually means temperature control only.

One effect of weather variations is on a spark source, and this has already been mentioned. The main effect of temperature variation on the spectrograph is to defocus

it to a degree which, though visually undetectable, may be enough to change the line widths and, consequently, their density. Here, temperature gradients are particularly troublesome because, by heating parts unequally, they affect different regions on the plate unequally. The slit and optical components may also distort to give rise to changes in line density. Apart from the spectrograph proper, temperature variations change the sensitivity of photographic emulsions and the parameters of electronic components in the source unit and the microphotometer. Humidity affects the sensitivity of photographic emulsions, too, not only by disturbing the formation rate of the latent image but also by absorbing radiation at the shorter wavelengths.

Optics. Considered a permanent fixture aligned, tested and sealed by the manufacturer, the optical system is ignored by spectrographers. Periodic checking is, nevertheless, recommended to avoid needless loss of precision. Improperly aligned external and internal optics, poor focusing, spectrographic aberrations, slit eccentricities all may give rise to drifting data.

The purpose of the external optics is to fill the spectrograph aperture with light and so obtain the maximum speed and resolving power. The images should be regularly inspected for vignetting of the source image by some aperture in the spectrograph (commonly the collimator). This is particularly important if a long slit is used (e.g. with a stepped sector or filter) since vignetting results in uneven illumination along the length of a line, affecting arc and spark lines in radically different ways.

Other causes of uneven illumination along the length of the lines are chromatic aberration of the optics and dispersion of any prisms in the optical system. (Here, it is interesting to note that B. & L. has recently changed its bi-prism system of dividing the beam to the gratings of the Dual Grating Spectrograph to a mirror system which elimi-

nates both problems.) In the commonly used three-lens system of illumination, the first lens, used for producing an intermediate image of the source, should be achromatically corrected to obtain uniform line illumination at all wavelengths.¹⁸

External optics are plagued with still another annoyance—arc wandering—and recently several novel corrective measures were proposed. One is the Linsenraster announced by Steinheil (West Germany), a lens system which produces an array of small intermediate images of the source instead of one as in the conventional three-lens system. As the arc wanders, each small image wanders but to a correspondingly smaller extent. Excellent control of arc wandering is said to be achieved in this fashion although at the expense of some loss of speed. A second system of correcting arc wandering is the use of a bi-prism as suggested by L. J. Linder (unpublished). An aperture is placed at the intermediate image position so that the image here is focused on the collimator. The apex angle of the bi-prism is so chosen that the image of the source, which would ordinarily fill the aperture in the screen, is split into two adjacent images with only half of each image falling in the aperture. When, as a result of arc wandering, one image moves out of the aperture, its twin moves into it from the other side. Light from all parts of the source is thus always entering the spectrograph but the intensity of illumination is, of course, reduced by a factor of two.

As has been mentioned under the heading of "Weather", improper focusing and changes in slit width disrupt relative intensities. They also adversely affect the sensitivity limit of the spectrograph because the maximum line-to-background ratio is reached only when the slit is made narrow enough to allow the natural line breadth to be recorded. Again the necessity of maintaining constant and optimum positioning of the optics is emphasized.

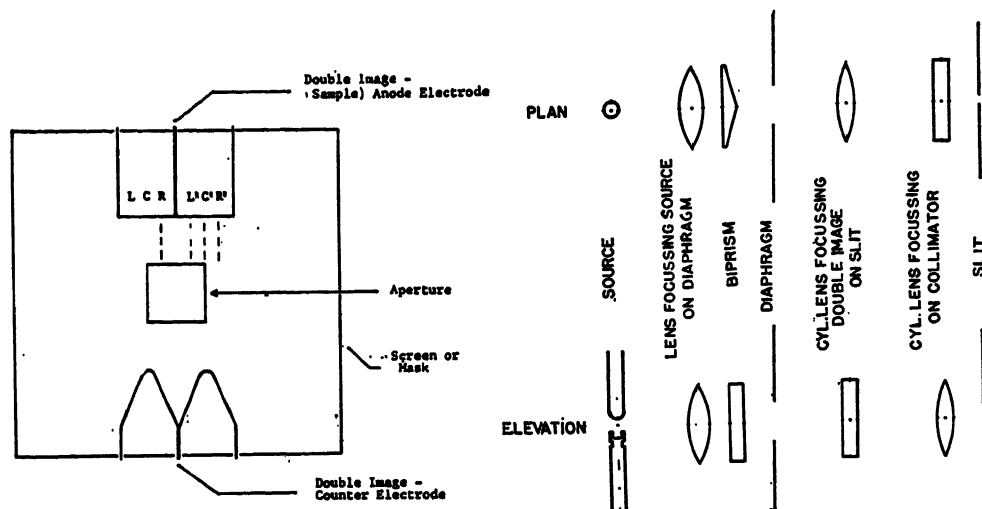


FIG. 1. Linder's use of a biprism system for suppressing arc wander.

Left: Inverted electrode images and aperture relationship.

Right: Optical system. A double image of the electrodes is focused on the aperture at the intermediate image position. As one image moves off-axis, the other returns.

Astigmatism and coma are two more optical imperfections which take their toll in accuracy. These are generally greater off axis: lines at the end of the plate are affected more than at the center. Astigmatism changes the intensity of a line by discarding some of the light vertically. Coma, on the other hand, widens a line asymmetrically. Accordingly, it is good practice for the spectrographer to maintain the same wavelength coverage on a plate for a given procedure to assure that all aberrations act on a particular line in the same way each time.

This precaution is particularly important if stigmatic mounts using mirror optics (or a concave grating) and a fairly wide focal field are used. Depending upon its position within the focal field, the photographically observed intensity of a narrow line may vary by as much as a factor of two.²²

Calculations. Evaluations of errors due to calculations made at various steps leading to the final % concentration in spectroscopy are, necessarily, indeterminate because so many calculations are graphical and, there-

fore, subjective. Reading and preparing a graph as well as the choice of scale, the thickness and closeness of fit of the line all depend on the skill of the operator. Here a recent trend is quite helpful. It is to convert scales wherever possible, to straight line graphs. Thus, the familiar S-shaped H and D curve appears on many calculating boards today as a straight line through the simple expedient of using a Seidel, or similar, transformation. Incidentally, such a transformation corrects only for the toe of the curve. The shoulder—at low transmittance values—results partially from scattered light in the microphotometer which enters the slit from portions of the spectrogram around the line itself. It is best for the spectrographer to steer clear of this region of high density in his work.

Analytical curves are normally straight but background may introduce a curved portion at values where the line and background begin to merge. To straighten out this region, background corrections are advisable and several have been proposed (Ref.

1, p. 79).^{*} Analytical curves are dependent on the presence of a third element and this effect can be minimized through the use of calculations involving ratios of concentrations rather than the calculations themselves. This, too, is explained by ASTM (Ref. 1, p. 74).

Photometry. Since quantitative spectrochemical analysis depends upon the evaluation of relative line intensities which, in turn, are obtained through photographic density measurements, its accuracy depends upon the methods used for calibrating emulsions and interpreting the data. From the standpoint of accuracy, a calibration procedure using two lines, two steps of a sector or filter is the best practical choice. The use of several steps requires a slit too long for uniform illumination. Other methods are hard to set up.

Under "Calculations," the value of using linear plots of the calibration data was stressed. Emulsion calibration curves measured with a modern microphotometer often yield linear plots on Seidel coordinate paper from about 4–90 % T. The lower limit is determined usually by scattered light in the instrument which originates largely from field illumination. There are two effects of this scatter: 1) the observed gamma will be lower than the true gamma; 2) at low transmittance values a false "saturation" of the H and D curve occurs, and the shoulder begins at lower densities than the true shoulder of the curve. For accurate work, densities above the beginning of the observed shoulder should be avoided. At high transmittances, the linearity of the Seidel plot depends upon the slope of the straight part of the H and D

curve (gamma). It is recommended that the emulsion should be developed to a gamma of approximately two (plus or minus about 0.3) when using Seidel calibration plots.²⁴ When this is not possible, the more general Kaiser function²⁵ may still be used to linearize the emulsion calibration curve.

The linearity of a microphotometer is another pertinent variable. By linearity is meant the ability of a microphotometer to reproduce the transmittance value of a spectral line regardless of its sensitivity setting. A simple test may be performed as follows:

Set the background reading in a clear portion of the plate at 100 % T. and read the transmittances of several lines at levels of about 5 %, 30 % and 70 % T. Next, reduce the overall light to the detector in some manner, by using a dimmer switch often provided on microphotometers or with a neutral filter (uniformly fogged film or smoked glass) taped to the condenser lens. Two or three such filters should be used having transmittances of about 25 %, 50 % and 75 %. Take readings of the spectral lines 1) without resetting the background at 100 % T; 2) after setting the background at 100 %. In all instances, the relative amount of light transmitted by the lines should be the same.

In practice, of course, variations are obtained when the above procedure is followed. A study of these will set practical limitations of the microphotometer for the spectrographer. Periodic checks are suggested as electronic components age.

Analogous to this electronic check is one which should be performed on the optics, especially with regard to focus. On many microphotometers the focus setting is much more critical than can be detected by the eye. In fact the best way of focusing the instrument is by setting it to the maximum effective density of a line:

Choose a line of around 30 % T. in the middle of a plate. The width of the line should be at least three times the width of

^{*} Caution should be exercised in applying the generally accepted methods of background correction. They are subject to photometric errors in measuring densities which are dependent upon the particular microphotometer used. In addition, work in progress at the Brookhaven National Laboratory²³, as well as some Russian work, has cast doubt upon the simple additivity of line and background intensities.

the scanning slit. Take several readings of the line at different focus settings and pencil a marking on the lens in the position of maximum density (best focus). Repeat for lines near the four edges of the plate. The optimum focus should be the same provided the carriage moves in a plane perpendicular to the optical components.

REFERENCES

1. "Methods for Emission Spectrochemical Analysis," ASTM (1957).
2. HURWITZ, J. K., *Spectrochim. Acta*, **9**, 3 (1957).
3. HURWITZ, J. K., *Spectrochim. Acta*, **12**, 211 (1958).
4. HURWITZ, J. K., *Appl. Spectroscopy*, **10**, 124 (1956).
5. CLARK, O. G., Pittsburgh Conference, 1959 (unpublished).
6. TINGLE, W. H., MATOCHA, C. K., *Anal. Chem.*, **30**, 494 (1958).
7. STRASHEIM, A., TAPPERE, E. J., *Appl. Spectroscopy*, **13**, 12 (1959).
8. BARDOCH, A., *Appl. Spectroscopy*, **10**, 183 (1956).
9. FELDMAN, C., ELLENBURG, J. Y., *Anal. Chem.*, **30**, 420 (1958).
10. OWEN, L. E., *Appl. Spectroscopy*, **12**, 178 (1958).
11. STALLWOOD, B. J., *J. Opt. Soc. Amer.*, **44**, 172 (1954).
12. JOENSUU, O., Pittsburgh Conference, 1959 (unpublished).
13. THIERS, R. E., VALLÉE, B. L., *Spectrochim. Acta*, **11**, 179 (1957).
14. HAMMAKER, E. M., POPE, G. W., ISHIDA, Y. G., WAGNER, W. F., *Appl. Spectroscopy*, **12**, 161 (1958).
15. FRY, D. L., SCHREIBER, T. P., *Appl. Spectroscopy*, **11**, 1 (1957).
16. KENNEDY, W. L., Pittsburgh Conference, 1959 (unpublished).
17. LANDON, D. O., Amer. Assoc. of Spectrographers meeting, Chicago, 1956 (unpublished).
18. MIELENZ, K. D., *Spectrochim. Acta*, **10**, 99 (1957).
19. ECKHARD, S., KOCH, W., *Arch. Eisenhüttenw.*, **28**, 731 (1957).
20. FELDMAN, C., Pittsburgh Conference, 1960 (unpublished).
21. SLAVIN, M., *Appl. Spectroscopy*, **14**, 82 (1960).
22. ARRAK, A., *Spectrochim. Acta*, **15**, 1003-1024 (1959).
23. SLAVIN, M., Pittsburgh Conference, 1960 (unpublished).
24. ARRAK, A., Proc. Coll. Spectr. Intern. VIII

(Lucerne 1959), special issue of *Chimia* (1960).

25. KAISER, H., *Spectrochim. Acta*, **3**, 159 (1948).

ARNO ARRAK AND A. J. MITTELDORF

ANALYTICAL EMISSION SPECTROSCOPY

Introduction. More and more physical methods are being used in today's industrial and research laboratories for analytical purposes. Analytical emission spectroscopy is one of these. In some cases it can be completely substituted for wet analytical chemical methods; in others it is a welcome adjunct since it makes possible identification of all metals and often nonmetallic elements as well. The particular advantage of the spectrographic methods in general are speed, remarkable sensitivity, accuracy, unequivocal identification and minimal material consumption. In addition to all this, either a photographic plate or a stripchart is retained as a document of the analysis which may be referred to at any time. Independently of the equipment used, the analytical procedures are in most cases the same and the variations from instrument to instrument may be considered minimal.

The professional spectroscopist has evolved because of the fairly complex instrumentation and the understanding of some of the mechanics of excitation, diffraction, optics and metallurgy that is required. His position may be considered midway between chemistry and physics. Since he operates in one of the fertile junction areas of the scientific mosaic, the professional spectroscopist often finds himself working in many and varied fields.

Historical. The discovery and application of a phenomenon in nature is dependent on persons who have one or a combination of the following gifts: luck, talent, perspicacity and perseverance. Spectroscopy, it has been said,¹ began when the flood ended, but man required thousands of years to learn to make practical use of it.

Excellent treatises on the history of spec-

troscopy are contained in the literature.¹⁻³ This may be summarized as follows.

It is generally conceded that the history of analytical spectroscopy begins approximately a century ago with the work of Bunsen and Kirchhoff and their discovery, by means of the spectroscope, of the elements rubidium and cesium, announced in 1860. Their work also marked the real beginning of astrophysics. The investigations of Kirchhoff and Bunsen were, however, based upon the work of many earlier investigators. In 1672 Sir Isaac Newton discovered the fact that "white" light is a composite of various colors. He also found that "rays of different colors undergo different degrees of refraction by a glass prism." He recognized that "when passing white light through a glass prism onto a screen, a regular and reproducible series of colors—the spectrum—may be produced."

Wollaston⁴ in 1802 placed a narrow slit before the prism and found that the spectrum thus produced from the light of the sun was crossed by black lines of varying distances from one another. Fraunhofer⁵ by 1817 had investigated the lines found by Wollaston and had mapped, according to an arbitrary scale and with improved instrumentation, 576 of the "Fraunhofer Lines" of the solar spectrum. Moreover he found and described the explanation of the phenomenon.

With even more improved instrumentation Sir John Herschel studied the spectra of several colored flames. He concerned himself particularly with flames into which he had introduced amounts of strontium and copper. In 1823⁶ he reported that "the colors thus contributed by different objects to the flame afford, in many cases, a ready and neat way of detecting extremely minute quantities of them."

This, then, is part of the basis upon which Bunsen and Kirchhoff built their work. In rapid succession additional new elements

were discovered by means of the spectroscope:

Thallium: in 1861 by Sir William Crookes

Indium: in 1863 by Reich and Richter

Gallium: in 1875 by Lecoq de Boisbaudran

Virtually all the rare earth elements as well as many other elements were discovered by means of, or with the aid of spectroscopy. Astrophysicists continued to be vastly interested in the field because it provided a prime means of studying the composition of celestial bodies. A large amount of work in instrumentation design was done by these groups.

Interest in the spectrochemical field, however, diminished quickly. Strangely enough, it apparently was the advance of electricity and the electric arc and spark which did much to discourage further work in the field. While the new excitation methods much improved the sensitivity, they also considerably increased the complexity of the spectra they produced. Many researchers decided that even the most tedious chemical analytical methods were to be preferred to the almost hopeless task of working one's way through such a maze of lines.

It must be remembered that all the early measurements were made visually in the visible spectrum. Some experiments were made with photography of spectra, but photography at that time was a highly unsatisfactory technique. Moreover, arbitrary scales were used to measure spectra until Watts began to develop the wavelength system. Ångström's work, a few years later, was much facilitated by the use of grating spectra after the invention and development of plane diffraction gratings by Fraunhofer in 1822. Rowland in 1882 developed the technique for the manufacture of concave diffraction gratings.

Between 1885 and 1924, when Loewe called it the "forgotten method," little was done in analytical emission spectroscopy. A few lone investigators carried on the work. Notable of these was de Gramont who, in

1907 published the "raies ultimes" of 59 elements; Kayser published the first volume of the "Handbuch der Spektroskopie" in 1900; and Twyman designed and built, at Hilger and Watts in England, a few spectrographs during that period. One of those instruments is reported to be still in daily use in a laboratory!

Gerlach in 1926 created new interest in analytical emission spectroscopy with the application of the "internal standard" principle. Since that time a multitude of papers has been published and continues to be published in many journals around the world.

About the mid-thirties industry began to cast about for faster, perhaps more accurate and certainly more sensitive methods of chemical analysis. Much credit is due here to Judd Lewis who helped to publicize the method by utilizing it to a large extent in his own laboratories. Most of his work, unfortunately, is buried in the confidential reports to his clients.

World War II gave much impetus to this "new" science, since speed, accuracy and simplicity became of the foremost importance. During the same period the instrumentation was developed to its present high state of perfection. Primarily because of the better production methods, but also because of the advent of excellent replica gratings, instrumentation is now available which is economically well within the reach of most laboratories.

The spectrographic method has emerged as a new tool for the analytical chemist. As it will be used to continually greater extent, the laboratory which lacks spectroscopy is at a very definite disadvantage, though of course it will never replace the analytical chemist.

Technical. The basic principle underlying the arc-spark emission spectrographic method may be described as follows: A minute part of the sample is vaporized and excited to the point of light emission. This may be done by means of an electric arc (5000°

to 8000°C) or spark (7000° to 20,000°C). Excitation parameters are selected according to the material to be analyzed. The light derived from the vaporized, excited material is dispersed into its component parts in the spectrograph. The medium of diffraction is either a prism or a grating. At the exit aperture this light is either photographed of a plate or film, or recorded by means on photoelectric devices. Since each element produces a spectrum (or rather a series of spectral lines of specific wavelengths), which is characteristic of itself, the identification of an element is possible by studying the lines according to their respective locations. Determination of quantity is made according to the intensity of the lines.

The flow sheet (Fig. 1) indicates the essential steps of the analytical process. It also indicates the multitude of different fields of science and technology which are involved in the generation of the final product: the analytical result. Sample preparation may involve problems of chemistry, metallurgy and machining practice. The excitation of the sample involves chemical reactions, thermodynamics, atomic physics and electronics.

The following is a simplified explanation of the excitation mechanism operating in the arc-spark and flame photometric light sources: The atom consists of a nucleus and a number of "orbiting" electrons surrounding the nucleus in stable energy levels. When all the electrons are at their lowest possible energy levels, the atom is considered to be in its "ground state." If this condition is disrupted by the introduction of a large amount of energy, the electrons are forced from their usual orbits to higher energy orbits—the "excited state." To return to their normal orbits, the electrons must release the energy with which they have been charged. They return from the excited state to the ground state in definite steps, releasing energy stepwise in the form of light. Each step accounts for the presence of a specific

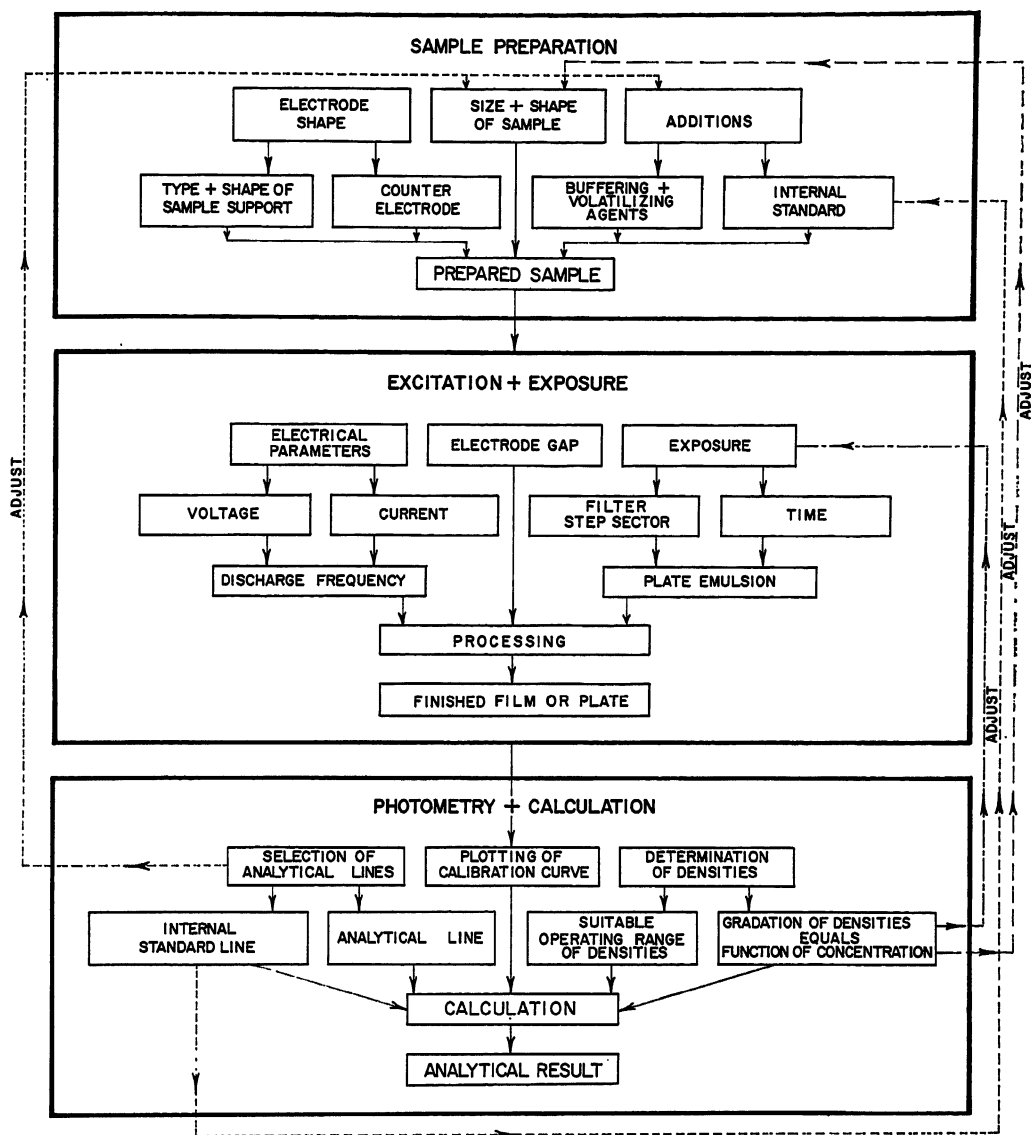


FIG. 1. Analytical emission spectroscopy flow sheet, indicating the many steps and variables involved in producing the final product: The Result.

frequency of light and hence the presence of a spectral line on the photographic plate.

In a sample composed of various types of atoms, e.g., iron, silicon and manganese, lines of each of these three elements will be present in the spectrum of the sample. When the concentration of iron atoms is greater than that of the silicon or manganese atoms,

the energy release from the iron electrons is much greater than that from the other two elements. Not only are more iron frequencies (lines) produced, but they are also of higher intensity than those of silicon and manganese. Identification of the elements present in a sample by the presence of their spectral lines is the basis for spectro-

EMISSION SPECTROSCOPY—LIGHT

graphic qualitative analysis; measurement of the intensities of the spectral lines permits quantitative analysis.

The spectrograph itself includes a wide variety of optical and mechanical problems; the photography of the resultant spectrum involves photographic technique, organic and inorganic chemistry, temperature control and mechanical design. In the case of direct-reading instruments, a maze of electronics is also involved.

The most important part of the spectrograph is the element which disperses the light. This may be either a grating or a prism. The use of prisms as light-dispersing media is well known. The grating is the finest piece of optical instrumentation made today and consists of a front-surfaced mirror with either a plane or concave surface. Into this surface grooves of precise angles and depths are cut with exact spacing. Commonly used gratings contain 15,000 and 30,000 grooves per inch and may be as much as 6 inches long. At the present writing there are perhaps ten ruling engines in the U. S., and these are by far the most precise mechanical instruments made.

The optical configuration of the entrance slit, lenses, grating or prism, and exit opening of different types of spectrographs varies with the manufacture of the instrument and the basic optical design used. The entire configuration of optics must be perfectly focused and aligned so that the spectral lines appear well spaced and properly dimensioned at the exit opening.

The most commonly used detector for the diffracted light radiation is a photographic film or plate. Special emulsions have been developed for this purpose; each covers a certain wavelength region and has varied speeds and resolving powers. The resultant spectrogram is therefore processed very much like any photographic emulsion. Photometry of the spectrum and calculation of the results require understanding of

mathematics, optics, electronics and mechanics.

Qualitative analysis on the spectrograph is done in the following manner: A powdered sample is mixed with enough graphite powder to make the mixture conduct electricity. The graphite powder also facilitates the vaporization of the very refractory constituents which may be present in the sample. The mixture is placed in a graphite cup which serves as the lower, usually positive, electrode in a DC arc. The arc raises the temperature in the cup to between 1500° and 3000°C, depending upon the electrode configuration. This causes the sample to be vaporized into the arc discharge zone above the electrode, where excitation takes place and the light emission from the sample occurs. Solutions may be vaporized from a cup or a flat graphite electrode and thus excited. Metallic powders loaded into a graphite cup need not, of course, be mixed with graphite powder since they are themselves conductive. Various methods have been described in the literature for the evaluation of the spectra thus obtained.

One of the most important problems is the identification of spectral lines. Many manufacturers of spectrographic equipment supply a "standard plate" which contains a large number of identified lines and which is made to correspond to the instruments they produce. Aligning such a standard film with the film containing the sample spectra is relatively easy and locating the analysis lines is thus facilitated. If such a standard spectrum is not available, one can be produced by merely exposing the pure elements which are of interest in a series of exposures on the same plate. The lines produced by the various elements in the sample spectrum can be identified in this manner.

For quantitative analysis, the densities of specific spectral lines of the desired element must also be determined. Most spectrographers use a microphotometer or densitometer for the measurement of line intensities.

In this instrument, the line to be examined and measured is aligned over (or under) a slit through which a quantity of light is focused from a carefully controlled light source. The amount of light passing through the slit and a clear section of the plate or film is arbitrarily considered 100 % transmission. When an opaque object is inserted between the light source and the slit, the galvanometer needle falls to 0 % transmission. More intense light emission by the excited sample results in denser (blacker) lines than less intense light emission. Therefore, the relative amount of light falling from the light source in the microphotometer through the line on the plate to the slit and to the photocell in the densitometer indicates a relative blackening of the film on the scale between 0 and 100. The measured transmission of the line therefore is in direct proportion to the amount of the element in the sample.

Despite the most careful control of the electrical discharge, small variations occur in the over-all exposure. For this reason all the transmission figures must be brought to a common denominator. Here the spectrographer uses the "internal standard" system. In a series of steel samples he reads the transmission of a given iron line. The iron in this case is so nearly constant in concentration that any error thus introduced is negligible. This method, however does give him a gauge of the relative density of the following exposures.

Once a relationship is established between the transmission readings of the internal standard line—in this case iron and the element line of the element to be determined—the ratio evolved represents a specific concentration. By using three or more standard samples, a concentration curve for the element can be constructed by plotting the ratios of element lines to internal standard lines versus concentration of the standard samples. The concentration of the element contained in the unknown sample can then

be determined by referring to this concentration calibration curve.

While this may seem complicated, one must recognize that many of the motions in this process need be done but once. This applies particularly to the industrial laboratory where a great number of similar samples are processed. As many as 16 exposures may be placed on a 35-mm film and as many as 40 on a 4 by 10-inch plate. Hence the time-consuming step of processing the film or plate is divided among the number of sample exposures on it. For example, the author has made as many as 66 determinations in less than 30 minutes in the laboratory of an aluminum smelter.

The analytical speed attainable with photographic plates is normally quite satisfactory. However, in a laboratory where large numbers of samples must be processed this speed is no longer sufficient. Samples must be analyzed in a total elapsed time of a few minutes. The furnace crew may be waiting for the results; hundreds of additional samples are waiting to be processed, and the pressure is on. For such cases, which occur more and more frequently in industry, a number of manufacturers resorted to automation and "direct reading" spectrographs were developed.

The optical system and excitation equipment of the direct readers are very much the same as for the photographic units. The difference occurs at the exit opening of the spectrograph. Here the light from individual element lines is isolated either by slits of the precise widths and in the precise locations where the desired spectral lines appear or by means of a complicated mirror system. Both methods accomplish the same objective, i.e., to focus the light of one spectrum line onto the plate of a photomultiplier tube. The photomultiplier, much like a photocell, transforms the radiant energy into electrical energy, while at the same time it multiplies the generated current a million times.

Numerous photomultipliers can be in-

stalled in an instrument to handle many different spectral lines. The current from the photomultipliers is fed, after amplification, to a precision condenser, which accumulates and "integrates" the current it receives until an automatic switching device discharges one condenser after the other and allows the current to flow to either a chart recorder or a series of milliammeters. By means of previously exposed standard samples, either the dials of the meters have been calibrated or a curve has been established for each reading on the chart recorder, so that the conversion of light intensity to concentration figures is completely automatic.

The visual analysis method, once the only form of emission spectroscopy, has virtually disappeared. It would appear that a large amount of work could be relegated to this method. Quick answers can be obtained in connection with such problems as materials mixups, sorting of materials, and the like, since most commonly used materials are sufficiently different from one another in the concentration of at least one element or in the presence or absence of elements. Even virtually untrained personnel can therefore contribute heavily to quality control problems in a plant. Good, inexpensive instrumentation which is easily operated and which is normally supplied with step-by-step instructions is now available.

Conclusion. The foregoing would indicate that analytical emission spectroscopy is a composite method, depending heavily upon the understanding and correlation of problems in many fields of science and technology. All the widely varied problems are closely related to one another and the variables in sampling, excitation, photography and measurement are all interdependent. One cannot consider the excitation source without also considering the kind of samples involved, the spectrograph, the photographic or electronic process and the photometry or measurement of the resultant spectra. Because of the virtually unlimited number of

combinations of electrical, optical, chemical and physical variables involved in spectrographic analysis, there are no "optimum" values to be given for any one parameter. In comparing instrumentation, one cannot call any one instrument superior to another without considering the balance of the train of instruments involved. In analytical emission spectroscopy one must always think in terms of combinations of instrumentation, combinations of conditions, combinations of circumstances.

REFERENCES

1. MEGGERS, W. F., *Spectrochim. Acta*, **3**, 5 (1947).
2. TWYMAN, F., "The spectrochemical analysis of metals and alloys." Chemical Publishing Co., Brooklyn, N. Y., 1941.
3. KAYSER, H., "Handbuch der Spektroskopie," Vol. 1, 1900.
4. WOLLASTON, W. H., *Phil. Trans.*, **92**, 365 (1802).
5. FRAUNHOFER, J., *Gilbert's Ann.*, **56**, 264 (1817).
6. HERSCHEL, SIR J. F. W., *Trans. Roy. Soc. Edin.*, **9**, 445 (1823).

THEODORE H. ZINK

APPLICATIONS OF EMISSION SPECTROSCOPY*

Present-day activity making use of line spectroscopy is concerned to an overwhelming extent with industrial applications in the areas of qualitative or quantitative analysis. Much of this activity has been related to automation in connection with the development of elaborate installations for direct reading of percentage compositions in the instance of continuous-sampling procedures. This section is limited to an attempt to mention a few of the guide lines that must be followed in analytical work and to list the more important literature surveys.

The unique character of the spectra associated respectively with the atoms or ions of an element immediately suggests spec-

* The tenth in a consecutively developed series of articles on the fundamentals of Optical Emission spectra: see *Introduction: Designation and Description of Spectra* for list of topics, p. 202.

troscopy as a means of identification. Spectrum analysis has indeed become firmly established as one of the most reliable techniques for identifying the elements making up the composition of a sample. Although its importance was recognized from the beginning of relatively precise wavelength determinations, the general acceptance and widespread use of the method were delayed for about a generation, or until the second decade of the century. When several spectra originating in a mixture of elements are superposed, there are obviously many very near coincidences between observed wavelengths and those listed for lines of various elements in catalogs of spectra, a situation leading to false identification in many instances. It therefore becomes necessary to establish criteria for the selection of lines to be used in identification. Most important of these criteria are the appearance of the sensitive or persistent lines of the element or elements sought, and the complete development with appropriate relative intensities of multiple groups.

For every spectrum there is at least one line that persists with vanishingly small concentrations. Such lines are called "persistent lines" or "raies ultimes." In general the persistent line is identifiable with the resonance line that arises from the transition to the ground state from the next higher state of equal multiplicity and opposite parity. A good example is the yellow sodium doublet. Listings of persistent lines are found in all handbooks on spectrum analysis and conveniently given in the "Key to the Periodic Chart,"¹ and the "American Institute of Physics Handbook."² If the persistent line is in a region inaccessible to the experimenter, possibly in the vacuum ultraviolet, other sensitive lines may be employed. In HgI, for instance, the resonance line is at 1849 Å, but the extremely intense intercombination line, 2536 Å, is usually available. Identification on the basis of a single line is generally suspect. A member of a multiple group

should be accompanied by the other related members. For instance, if a line were found in the position of 4047 Å of HgI it would not be proper to claim the identification without the presence of 4358 and 5461.

Quantitative spectrographic analysis, while simple in concept, requires experimental methods of extreme sophistication. In general it is necessary to establish a relationship between concentration of a component and intensities of characteristic lines arising from that component. This may involve comparison of the test specimen with a series of precisely compounded standard samples of varying concentration. Among the requirements of the experimental routine are: Careful preparation of test specimens in the form of arc or spark electrodes both as to geometric form and freedom from contamination; operation of power supply units in precisely controlled fashion; handling all items of the photographic procedure under complete control, including specification of plate types, precise timing of exposures, and control of physical environment of exposure and processing; and finally use of correct calibration processes to arrive at the relationship between optical density and spectral intensity. In contrast with the methods of infrared absorption spectrophotometry used mainly for the analysis of organic compounds in which the components occur in concentrations of the same order of magnitude, spectrochemical analysis using the methods of emission spectroscopy finds its principal application in the detection of trace elements in metallurgical specimens.

The development of spectroscopy in its application to chemical analysis may be traced from an experimental program at the National Bureau of Standards first reported in 1922.³ Accompanying the spectacular growth in the industrial utilization of the art, there has been a large-scale output of publications. References of a general character include *Foundations and Methods of Chemical Analysis* by the Emission Spec-

trum by Gerlach and Schweitzer,⁴ and Chemical Spectroscopy by Brode.⁵ The responsibility for surveying and indexing this enormous selection of material has been assumed by W. F. Meggers and B. F. Scribner of the National Bureau of Standards. In their Index to the Literature of Spectrochemical Analysis,⁶ which has appeared in several parts, over 5000 papers have been listed and mostly abstracted. The same authors have prepared the articles on Emission Spectroscopy in *Analytical Chemistry*,^{7, 8} in the series of biennial surveys dealing with spectrochemical methods. References to the literature must also include the most extensive compilations of spectral lines in order of wavelengths. These include the MIT Tables⁹ and Hauptlinien¹⁰ by Kayser and Ritschl. The most complete work on spectroscopy covering both experimental techniques and compilations of data is "Handbuch der Spektroskopie" by Kayser and Runge, in late editions by Kayser and Konen.¹¹ Much of the material is now superseded by new data.

Atomic spectroscopy finds extensive and important applications in astrophysics. With a few notable exceptions, including O-type stars, certain classes of gaseous nebulae, and instances of excited gaseous material distributed in space, all of which are emission sources, celestial objects display absorption spectra similar in some respects to the Fraunhofer spectrum of the sun. For the most part these absorption spectra originate in clouds of cooler gases surrounding stars which in turn are emitting a continuous spectrum having a spectral distribution determined by temperature. In simple tests, observation of stellar spectra provides two classes of information. First identification of the atomic, ionic, or molecular origin of the lines determines unquestionably what elements are present in the stellar atmospheres. In the second place, interpretation of the Doppler effect provides clues to stellar motions. According to this principle, the wavelength of a given radiation shows an appar-

ent increase for a receding emitter and a decrease for an approaching one. This is quite analogous to an acoustic phenomenon manifesting itself in the rise or fall of pitch from an approaching or receding sound emitter.

Detailed analysis of the Doppler effect permits description of the orbital characteristics of pairs of stars, known as spectroscopic binaries that are linked together under gravitational forces in a mechanical system. Similar Doppler-effect studies of spectra of galaxies provide all available evidence for the "red shift" on which the hypothesis of the expanding universe is based.

The detailed study of the spectra of stars permits sorting them into groups, generally known as temperature classes. The characteristics of these classes designated by letters, O, B, A, F, G, K, M, R, N, S, with appropriate subgroups, provide the basis for current theories of stellar evolution. The classification is in part determined by the temperature-conditioned spectral distribution of the background and in part by the superposed Fraunhofer spectrum. In this system the sun is described as a class-G star, a class characterized by temperatures of the order of 5000° absolute and an abundance of elements of the first long period. For a detailed treatment, reference is made to well-known works on astrophysics such as that of Rosseland.¹²

The material in this section emphasizes the diversity of the uses of experimental spectroscopy ranging from the detection of minute traces, as small as one part in ten million in the instance of the alkalis, to the determination of the composition or characteristics of remote celestial objects. It is thus perhaps the most universal of all subjects combining in its application the extremes of our concepts of magnitudes, the dimensions of the atom and of the universe.

REFERENCES

1. W. F. MEGGERS, "Key to the Periodic Chart of the Atoms," W. M. Welch Mfg. Co., Chicago, 1959.

2. "American Institute of Physics Handbook," McGraw-Hill, New York (1957).
3. W. F. MEGGERS, C. C. KIESS AND F. J. STINSON, *Sci. Pap. Bur. Stand.*, **18**, 235 (1922).
4. W. GERLACH AND E. SCHWEITZER, "Foundations and Methods of Chemical Analysis by the Emission Spectrum," Hilger, London, (1932).
5. W. R. BRODE, "Chemical Spectroscopy," 2nd Ed., John Wiley and Sons, New York (1943).
6. W. F. MEGGERS AND B. F. SCRIBNER, "Index to the Literature of Spectrochemical Analysis: Part I, 1920-1929; Part II, 1940-1945; Part III, 1945-1950; Part IV," (in Press); *Am. Soc. Test. Mat.*, Philadelphia, Pa.
7. BOURDON F. SCRIBNER, *Analytical Chemistry*, **30**, 596 (1958).
8. Wm. F. MEGGERS, *Analytical Chemistry*, **28**, 616 (1956), **26**, 54 (1954), **24**, 23 (1952), **22**, 18 (1950), **21**, 29 (1949).
9. "M.I.T. Wavelength Tables," John Wiley and Sons, Inc., New York (1939).
10. H. KAYSER AND R. RITSCHL, "Tabelle der Hauptlinien der Linienspektren aller Elemente," Springer, Berlin (1939).
11. KAYSER-KONEN, "Handbuch der Spektroskopie," Hirzel, Leipzig (1905-1933).
12. S. ROSSELAND, "Theoretical Astrophysics," Oxford, London (1936).

CURTIS J. HUMPHREYS

ATOMIC EMISSION SPECTRA, ANALYSIS OF*

In a paper published in 1951,¹ Meggers listed the three principal goals of research in atomic spectra paraphrased as follows: (1) Grouping of the energy levels into spectral terms and correlating these terms with electronic configurations in order to establish the electronic structure of atoms and ions in both normal and excited states; (2) Recognition of series and extrapolation of these series to the ionization limit to give an accurate value of the force that binds the electron to the atom or ion; (3) Study of hyperfine and isotope structure to determine the mechanical, magnetic and quadrupole moments of nuclei, and to make progress in the understanding of nuclear structure.

* The eighth in a consecutively developed series of articles on the fundamentals of Optical Emission Spectra: see *Introduction: Designation and Description of Spectra* for list of topics, p. 202.

In any energy level analysis the first step is obviously to obtain the levels from the description of the spectrum. A prerequisite to the analysis of a spectrum is that the spectra originating in the various ions of the same element be sorted out, so that the description to be used contains only data associated with emitters of a single category. Experimentally established criteria must be utilized to establish this differentiation. Most of the experimental devices are listed as follows: (1) Progressive thermal excitation illustrated by the furnace technique developed by A. S. King. (2) Differentiation between the spectra originating in arc and spark discharges. (3) Suppression of spectra of ions of higher stages by introduction of varying amounts of inductance into the circuit in which a spark is operated. (4) Geometric differentiation in the discharge pattern. Illustrations are the increase in excitation outward along a radius in a cylindrical tube enclosing an electrodeless ring discharge, also the higher excitation associated with short lines originating at the electrodes of an arc. (5) Use of discharges in which the excitation is limited by the ionization potential of the carrier gas, illustrated by the hollow cathode. (6) Use of sources of inherently low excitation such as the microwave-excited electrodeless tube.

In the instance of complex spectra without obvious regularities, it is customary to comb the wave number list for a recurrence of differences. This permits an arrangement of the wave numbers into what is called a supermultiplet or quadratic array consisting of rows and columns separated by differences constant to within an adopted tolerance. This permits the setting up of two new sets of numbers parallel respectively to the rows and columns which, when differenced, yield the wave numbers, also differences corresponding to the gaps in the array. The derived numbers are on an arbitrary scale conveniently set so that the smallest is zero. In this way we arrive at two sets of levels of opposite parity. Actually this method was

used by Snyder² twenty years before intensive activity in the analysis of complex spectra was set in motion following the discovery of multiplets by Catalan.³ The described procedure suffers from an obvious defect inherent in the possibility of fortuitous regularities. This makes it important that high precision of measurement of wavelength be attained particularly in densely populated spectra, in order to keep the tolerance for accepting differences as small as possible. The method is also long and tedious if carried out by manual computing methods. Fortunately, efforts to program the problem for automatic digital computers are making gratifying progress. The program of improving wavelength measurements is tied in with extending and improving the quality of the system of wavelength standards, also with improvements in equipment including use of gratings of larger area and higher resolving power.

When the array is set up, support for the choice of j -values is provided by the location of the gaps, having in mind the selection rules, and by relative intensities. In some instances wave numbers predicted in the gap positions may be filled in by new observations, particularly in spectral regions not previously covered.

In assigning quantum designations to the experimentally determined levels, it must be kept in mind that the possible sets of terms are limited by a very restricted choice of electron configuration. It has been pointed out that term arrays for equivalent electrons are well known. Terms resulting from the addition of other electrons to an equivalent group are predicted by using the vector scheme. The final arbiter for establishing the quantum numbers associated with each of two combining levels is the Zeeman effect. To be utilized advantageously, the pattern should be completely resolved and the character of the coupling established. The rare-earth character of uranium, resulting from the presence of f -electrons in the external

configurations, was first established by Zeeman-effect observations by Kiess, Humphreys, and Laun.⁴ Zeeman-effect observations have always been handicapped by difficulties associated with obtaining large steady magnetic fields. Most Zeeman-effect data contained in older publications were obtained with maximum field strengths obtainable with electromagnets equipped with core and pole pieces of ferromagnetic material. These fields ranged up to 35,000 oersteds. Fields of the order of 100,000 oersteds have been realized with the Bitter magnet at the Massachusetts Institute of Technology.

Long series are not of frequent occurrence in many-electron spectra. If, however, only two members of a series starting with the ground state can be observed, a Rydberg interpolation will give a fair estimate of the ionization potential. Three or more members will permit setting up a Ritz equation and yield a very nearly correct value.

REFERENCES

1. WILLIAM F. MEGGERS, *J. Opt. Soc. Am.*, **41**, 143 (1951).
2. C. P. SNYDER, *Astrophys. J.*, **14**, 179 (1901).
3. M. A. CATALAN, *Phil. Trans. Royal Soc.*, **A223**, 127 (1922).
4. C. C. KIESS, CURTIS J. HUMPHREYS, AND DONALD D. LAUN, *J. Research N.B.S.*, **37**, 57 (1946).

CURTIS J. HUMPHREYS

BOHR THEORY: INTRODUCTION*

The first real breakthrough in the interpretation of atomic spectra in terms of a model or physical concept of the mechanism of the emitter came in a series of publications by Niels Bohr in 1913.¹ This theory was based on two postulates, namely: (1) the existence of atomic stationary states, and (2) the identification of the frequency of the

* The third in a consecutively developed series of articles on fundamentals of Optical Emission Spectra: see *Introduction: Designation and Description of Spectra* for list of topics, p. 202

monochromatic radiation, associated with a spectral line, with the energy difference of two states divided by Planck's constant h . The model of the atom envisaged to account for the radiationless stationary states was conceived as a planetary system consisting of a central positively charged nucleus surrounded by negatively charged electrons circulating in orbits according to Kepler's laws. In the simplest approach to the theory, the concept of the hydrogen atom, there was only one planetary electron circulating about the particle possessing unit positive charge, now called the proton. The stationary state was assumed to persist as long as the electron remained in a fixed orbit. It was further assumed that no radiation was emitted during the lifetime of this state. Inconsistency of the radiationless state with an electrodynamic interpretation was one of the essential weaknesses of the theory that finally contributed to its abandonment as representing physical reality. Its usefulness for purposes of instruction is still recognized, because it provides a means of visualizing atom mechanics. The fallacy lies in the fact that, according to the laws of electrodynamics, an electron could not be maintained in an orbit under Coulomb forces without a constant expenditure of energy and, conversely, without such a supply of energy, it would be expected to spiral down with the accompaniment of emission of radiation of varying frequency. The emission or absorption of energy implied in the second postulate is associated with a jump, sometimes called a quantum switch, from one stationary state to another. Absorption is associated with a jump in a direction to increase the energy, emission with a loss in energy, or, according to the model, a switch from an orbit of greater to one of lesser energy. No mechanism has been proposed to explain how these quantum jumps take place. Incontrovertible evidence establishes the existence of stationary energy states apart from any concept of a physical model.

In strict justice to his predecessors, it should be noted that Bohr's theory was not built up of wholly new concepts in every particular. The open structure of the atom was clearly indicated by the α -ray experiments of Rutherford and Chadwick. Planck's quantum theory, to account for the emission and absorption of continuous radiation, was based on the quantized behavior of an array of harmonic oscillators. Finally the empirically established spectral terms of Rydberg constituted a natural stepping stone to the concept of energy states.

The simple introductory aspects of the Bohr theory are regarded as fundamental and indispensable to even a casual familiarity with atomic spectra and their interpretation. The immediately following material is intended to serve only as such an introduction and is inserted with the understanding that the development of the theory may be followed in any desired degree of completeness and rigor by using a selection from the general references.

The simplest possible model of the hydrogen atom, subject to several later modifications, envisages an electron moving under the attraction of a Coulomb force field in a circular orbit about the exact center of the positive nucleus. Mechanically this requires the assumption of an infinitely large mass at the center. The electron of mass m is held in its orbit by the Coulomb force between the unlike charges balancing the centrifugal force set up by the motion. If we call the orbital radius a , the velocity along the orbital path v and the angular velocity ω , the centrifugal force is variously represented as

$$\frac{mv^2}{a} = mv\omega = ma\omega^2$$

The Coulomb force by elementary electrostatics is Ze^2/a^2 , where Z is the number of positive charges on the nucleus. Accordingly,

$$ma\omega^2 = \frac{Ze^2}{a^2}$$

or

$$ma^3\omega^2 = Ze^2$$

At this point some means must be found to specify a set of permitted orbits. The quantum condition here introduced, which may be considered as an additional assumption of Bohr's theory, is that the orbital angular momentum must be equal to an integral number of units of the quantity $\hbar/2\pi$, that is, $p = (nh/2\pi)$ where $\hbar$ is Planck's universal constant of action. This represents a special case of a more general treatment developed in Planck's radiation theory, there applied specifically to the harmonic oscillator. In the general case of a mass particle of momentum p and position q , where these are generalized coordinates that describe some form of cyclic pattern, executed in a phase space, the derived quantum condition for each degree of freedom of the system is that the value of the cyclic or phase integral must be a whole multiple of $\hbar$.

This is formulated

$$J_k = \oint p_k dq_k = n_k \hbar.$$

It is important to note that the simple rotator is quantized not in energy quanta, but in quanta of angular of momentum. The evaluation of the phase integral, since the angular momentum is constant for uniform circular motion, reduces simply to $2\pi p$. It is to be emphasized that this is only a starting point in the development of atomic structure in relation to the features of emission spectra. Subsequent modifications of the model require additional degrees of freedom for which new quantum conditions are imposed, but the procedure follows that outlined in the preceding discussion. This method of introducing the quantum condition appears somewhat arbitrary and artificial. The new quantum mechanics contain a more satisfactory treatment since the quantum states appear naturally as characteristic solutions of the Schrödinger wave equation.

No attempt is made in this article to include a discussion of modern quantum mechanics. The wave mechanics as developed by Schrödinger and the matrix mechanics of Dirac provide a rigorous method of introducing the quantum conditions. These methods develop a formal treatment of the concept of the essentially dual nature of matter and energy according to which both matter and radiation possess both particle and wave properties. In place of the model representing the atom as a system of orbits, the position of the electron is represented as a probability density function. In the following sections the orbital model, which may be thought of as an approximately equivalent mechanical system, is retained for purposes of discussion.

Returning now to the problem of the described model, the angular momentum p is given by

$$p = \frac{nh}{2\pi}$$

Therefore

$$ma^3\omega = \frac{nh}{2\pi}.$$

By a simple algebraic operation combining this last equation with the expression for the attractive force we obtain expressions for the values of the radius a , the orbital velocity v , the angular velocity ω and the period T in terms of n , as follows:

$$v = a\omega = \frac{2\pi Ze^2}{nh},$$

$$a = \frac{n^2 \hbar^2}{4\pi^2 m Z e^2}, \quad \omega = \frac{8\pi^2 m Z^2 e^4}{n^3 \hbar^3}$$

$$T = \frac{2\pi}{\omega} = \frac{n^3 \hbar^3}{4\pi^2 m Z^2 e^4}$$

n is an integer, 1 or more, associated with the 1st, 2nd . . . n th Bohr circle. These expressions are in conformity with Kepler's laws.

To determine the radius of the first Bohr

orbit of hydrogen, which corresponds to the normal state of the atom, we set n equal to 1 and substitute the accepted values of the physical constants in the formula for a . We obtain $a_1 = 0.528 \times 10^{-8}$ cm, a value in excellent agreement with that obtained from collision experiments.

Another relationship of considerable physical significance is the ratio of the orbital velocity to the velocity of light. When calculated for the first Bohr orbit, this relationship, designated α , is formulated

$$\alpha = \frac{v}{c} = \frac{2\pi e^2}{ch}.$$

This is called the fine-structure constant and has the value $7.28 \cdot 10^{-3}$ or in reciprocal form $1/137.29$. It appears in all formulations for the fine structure of hydrogen lines, also in formulas for the separation of multiple groups of lines, doublets, triplets, and so forth. Configurations of the latter type are also designated fine structures for historical reasons, although in complex spectra they are not necessarily narrow.

We now come to the essential objective of this simplified derivation, namely the evaluation of the energies associated with the respective Bohr orbits. The energy of the electron in its orbit is equal to the sum of the potential and kinetic energies. The potential energy arising from Coulomb attraction is

$$E_{\text{pot}} = \frac{-Ze^2}{a} = \frac{-4\pi^2 me^4 Z^2}{n^2 h^2},$$

the latter form being obtained by substitution of the value of the radius, already listed. The negative sign is used because the force is one of attraction, it being necessary to perform work to move the electron away from the nucleus. The choice of this algebraic representation entails that the energy becomes zero for infinite separation. This apparent paradox of negative energy tends to create some confusion, but actually causes no difficulty in actual problems because, as we shall see, we are always dealing with differences of energy.

In a Coulomb field the kinetic energy is in general represented by

$$E_{\text{kin}} = -\frac{1}{2} E_{\text{pot}}.$$

This may be confirmed in this instance by substituting the value of the orbital velocity in the elementary kinetic energy formula,

$$E_{\text{kin}} = \frac{m}{2} v^2 = \frac{2\pi^2 me^4 Z^2}{n^2 h^2}$$

The total energy,

$$W = E_{\text{kin}} + E_{\text{pot}} = -\frac{2\pi^2 me^4 Z^2}{h^2} \cdot \frac{1}{n^2}$$

We now return to Bohr's second postulate, that the frequency of a spectral line is proportional to the difference between two energy states; that is, calling actual frequency $\bar{\nu}$,

$$h\bar{\nu} = W_m - W_n.$$

Suppose we are dealing with emission in which there is a transition from a state of greater to one of lesser energy. In terms of the convention of signs, W_n , although associated with lesser actual energy, is associated with a larger negative number. Let the quantum number appropriate to W_m be m and that associated with the W_n be n . We obtain

$$\bar{\nu} = W_m - W_n = \frac{2\pi^2 me^4}{h^2} Z^2 \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

In this context the quantum number m is associated with the initial state, n with the final. If instead of actual frequency we use the wave number ν where $\nu = \bar{\nu}/c$, that is frequency divided by the velocity of light,

$$\nu = \frac{2\pi^2 me^4}{h^2 c} Z^2 \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

If we make the substitution

$$R = \frac{2\pi^2 me^4}{h^2 c}$$

$$\nu = RZ^2 \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

EMISSION SPECTROSCOPY—LIGHT

This is identical with the Balmer formula in the form used by Rydberg. R is identified with the Rydberg constant. The value of this constant calculated in terms of the known values of physical constants in the expression

$$R = \frac{2\pi^2 m e^4}{h^3 c}$$

is close enough to the Rydberg constant derived from experimental data that it represents an almost spectacular confirmation of the theory. The derivation of the Balmer formula and the interpretation of the Rydberg constant were only the first of many successes of the Bohr theory in accounting for the physical features of spectra, both hydrogenic and more complex types.

The accuracy of the value of the Rydberg constant obviously depends on how well the physical constants appearing in the expression are known. Since spectroscopic measurements are among the most precise attainable, use of an experimental value of R for a hydrogenic type atom may be considered as an alternative means of arriving at the other constants. The value derived for R on the assumption of infinitely heavy nucleus may be modified readily by considering the effect of finite mass of the nucleus about a common center of gravity. In this instance it is correct according to classical mechanics to replace the electron mass m by a reduced mass, designated μ , where

$$\mu = \frac{m}{1 + \frac{m}{M}}$$

In this instance M is the mass of the nucleus. In an experimental determination, as in the instance of hydrogen, it is the Rydberg constant appropriate to the element that is found. This may be transformed into the value for infinitely heavy nucleus by using the formula,

$$R_A = \frac{R_\infty}{1 + \frac{m}{M}}$$

One of the interesting puzzles solved by making use of the simplified form of the Bohr model was the interpretation of a series of lines first observed in certain stellar spectra, and named for its discoverer the Pickering series. This series, originally believed to originate in some form of hydrogen unknown in laboratory sources because the alternate members coincided with the Balmer lines, was explained by Bohr as originating in ionized helium. Here, of course, $Z = 2$, and the previously derived formula for the wave numbers in a hydrogenic series becomes

$$\nu = 4R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

In the Pickering series n_1 is 4 and n_2 takes running values 5, 6, 7, . . . As in the instance of hydrogen other series are possible that are given respectively by the choice of n_1 as 1, 2, or 3, with n_2 starting with running values larger by 1 in each instance. All of these series have been observed.

The laboratory counterpart of the Pickering series was first observed by Fowler in 1914 at the Imperial College in London. Precise measurements of the wavelengths of the members of this series showed small but measurable differences between the wavelengths of the members of the Balmer series of hydrogen and the lines of the series of the spectrum of ionized helium that fall in the same locations. It was shown that these wavelength differences could be explained completely on the basis of the difference in nuclear mass associated with hydrogen and helium. The presently accepted values of the Rydberg constant that are applicable to this problem are quoted as follows:^{2, 3}

Rydberg constant for infinite mass,

$$R = 109737.31 \pm 0.01 \text{ cm}^{-1}$$

Rydberg constant for hydrogen,

$$R_H = 109677.58 \pm 0.01 \text{ cm}^{-1}$$

Rydberg constant for helium,

$$R_{He} = 109722.40 \pm 0.05 \text{ cm}^{-1}$$

The next hydrogenic spectra in order may be similarly formulated

$$\text{Li III, } \nu = 9R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\text{Be IV, } \nu = 16R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

These were discovered in 1930 by Edlén and Ericson⁴ at the University of Lund. Eventually the sequence was extended by Edlén and his students as far as O VIII, the last being contributed by Tyrén in 1940. This is an example of what is called an isoelectronic sequence, a set of spectra originating in ions of elements of ascending order of atomic number, but with identical electron configurations.

Another striking example of the nuclear mass effect is the displacement of lines originating in deuterium, the isotope of hydrogen of atomic mass 2, discovered by Urey, Brickwedde, and Murphy in 1932.⁵

In series calculations involving non-hydrogenic spectra, R_∞ is generally employed, the mass correction being taken care of by adjustment of the series constants.

Even when first introduced, the model envisioning circular orbits was regarded as an oversimplification. Particularly in the hands of Sommerfeld it assumed a more general form in which the orbits were represented by Keplerian ellipses, among which the circle could be included as a special case. The energy associated with orbital motion in a circle of given diameter is equal to that in an ellipse having a major axis for the same length. Hence the introduction of ellipses should not affect the values of the hydrogenic energy levels or the pattern of the spectrum. There is, however, an expected relativistic mass effect associated with the change of velocity near perihelion. This should lead to a precession of the perihelion analogous to that occurring in the orbit of the planet Mercury. The relativistic correction derived by Sommerfeld accounted for the observed fine structure of hydrogen lines

with reasonable precision although further refinements were eventually needed. In accordance with selection rules that came out of subsequent elaboration of the theory no transitions would be possible between hydrogenic orbits if they were all circular. It is necessary that transitions be between orbits of different eccentricity. As previously explained, the formalization of the quantum conditions, which is attributed independently to Wilson and Sommerfeld, requires that each degree of freedom be quantized separately. In an elliptic orbit the two degrees of freedom are associated with the azimuthal angle and radius drawn from the focus which describe the position of the electron in polar coordinates. Application of the quantum conditions leads to the introduction of two new quantum numbers called the azimuthal and radial quantum numbers and originally designated k and r . These are integers connected by the relation $k + r = n$. The significance of n has been discussed. Later developments, particularly those associated with the introduction of wave mechanics, have led to the replacement of k by a quantum number designated l , which has the same general significance, but is 1 less than k in a given situation. It turns out that the ratio of k to n is the same as that of the minor to major axis of the ellipse, with the result that when $r = 0$, or $k = n$ the orbit is circular.

In order to harmonize formulations derived on the basis of the orbital model with purely quantum-mechanical developments it is frequently necessary to replace k by $\sqrt{l(l+1)}$, usually designated l^* . The representation of the angular momentum quantum vector as $l^*\hbar/2\pi$ is particularly important in the treatment of multiple-term structure and Zeeman effect.

Although the introduction of elliptical orbits made no large-scale modifications of the structure of hydrogenic spectra, the orbital form is quite important in the instance of atoms possessing more than one

electron. In a relatively simple case, such as an alkali, we envision a single valence electron circulating about an inner core or cloud of electrons surrounding the nucleus. The energy will be vastly different depending on whether the electron remains outside or penetrates the core even when orbits are compared that have the same major axis. This is, of course, a consequence of the screening of the nucleus by the extranuclear structure. The effective nuclear charge is therefore subject to significant variation. The small differences that appear as fine structure in hydrogen have as their counterpart the various spectral series that were found first in the alkalis and designated in empirical fashion, principal, sharp, diffuse, and fundamental.

REFERENCES

1. N. BOHR, *Phil. Mag.*, **26**, 476 (1913).
2. "American Institute of Physics Handbook," McGraw-Hill, New York (1957).
3. H. E. WHITE, "Introduction to Atomic Spectra," McGraw-Hill, New York (1939).
4. B. EDLÉN AND A. ERICSON, *Z. Physik*, **59**, 679 (1930). Additional references to this sequence of spectra are to be found in *Atomic Energy Levels*, Vol. I.
5. H. C. UREY, F. G. BRICKWEDDE AND G. M. MURPHY, *Phys. Rev.*, **40**, 1 (1932).

CURTIS J. HUMPHREYS

CALCULATION EFFECTS ON ACCURACY. *See* ACCURACY IN SPECTROCHEMICAL ANALYSIS, p. 99.

CERAMICS ANALYSIS: GENERAL APPLICATION

The many ceramic compositions represented by glass, porcelain enamel, glazes, refractories, whitewares, and structural clay products make interesting problems for spectrochemical analysis since most of them are silicates which defy rapid wet analysis. Porcelain enamel frit alone may contain over one per cent of some of twenty-five oxides; twelve of these oxides may in turn occur over the ten per cent level. In addition,

other trace elements may be present, representing much of the periodic table, and exceeded only by geochemical samples in diversity.

No monograph on ceramic spectrochemical methods is available, but L. H. Ahrens' "Quantitative Spectrochemical Analysis of Silicates" (Addison-Wesley, Cambridge, 1955) is an excellent source of information on the d.c. arc analysis of natural silicates. The best collection of methods is in the A.S.T.M. "Methods for Emission Spectrochemical Analysis" (1957). Articles on British, German and Russian work appear to be fully as prominent as American articles. Prominent workers include E. K. Jaycox, R. W. Smith, W. Ward, and F. Hegemann.

Considerable analytical work is performed on the raw materials themselves, but analysis of the finished compositions may be important. Unlike metals manufacture, analyses and composition alterations are not attempted on the molten batch of glass or product being fired. The simplest analyses involve mixing the powdered sample with graphite and other diluents or buffer material to render the sample more conducting, and burning to completion in a d.c. arc, generally at 10 to 15 amperes. The diluents produce a more stable arc and decrease the reversal of some of the element lines. Volatility differences of the constituent oxides are important in determining arcing conditions and the selection of an internal standard.

Semi-quantitative methods are useful because they may be applied to a wide variety of compositions. If the analysis is to be made quantitative, standards should resemble samples rather closely. Most quantitative methods are for oxides below five per cent. The precision attained at higher percentages is often insufficient, although some methods are designed for high percentages.

In addition to d.c. arc methods, solution-spark and briquet-spark methods are often used. The solution follows a fusion of the sample and may be sparked directly or after

drying. Precision is improved with some sacrifice in speed and sensitivity. Samples fused with carbonate and borate and briquetted with graphite make excellent samples for sparking and even direct reader analysis, as exemplified by the general method of W. H. Tingle and C. K. Matocha (*Analytical Chemistry*, **30**, 494, 1958).

Emission spectrographic analysis can be used for a complete oxide analysis of ceramics. Glasses containing phosphates and fluorides require additional exposures. A more sensitive emulsion (such as Eastman 103-0) than is normally used will greatly improve the detection of the 2534–2554 Å phosphorus quartet. An emulsion sensitive in the visible region facilitates detection of traces of alkalis and permits the determination of fluoride, making use of calcium or strontium salt additions and the measurement of CaF or SrF bandheads.

D. C. SPINDLER

CERAMICS ANALYSIS TECHNIQUES*

The numerous methods that have been described for the spectrographic determination of both trace and major constituents on non-conducting materials can be divided into three principal groups according to the way in which the sample is prepared for and introduced into the discharge:

(1) The finely ground material, or material mixed with another substance which acts as an internal standard and/or spectrographic buffer, is placed in a cavity made in the lower of two pure graphite or carbon electrodes, usually the anode, and is then volatilized in a D.C. arc.

Ahrens¹ described methods of this type which he used in the determination of trace constituents in rocks. Kvalheim² used beryllium carbonate as an internal standard and added in addition NaCl and graphite as buffers. Jaycox³ estimated major constit-

uents by dilution of the sample with graphite and CuO, which served both as a buffer and as an internal standard, while Fitz and Murray⁴ investigated a technique for very small specimens, Ba(NO₃)₂ being used as internal standard and (NH₄)₂SO₄ as buffer. More recently Anthony, Chandler and Huckaboy⁵ described, for the determining of SiO₂ present as a major constituent, a method in which the sample is mixed with large amounts of Ge powder and graphite.

(2) The finely ground sample is mixed with briquetting graphite, and internal standard and a flux, and pressed into a briquette. A controlled spark discharge is used for excitation. Zander and Terry⁶ mill 0.3 to 0.75 g of sample with 1 g of graphite and 0.25 g of internal standard, which is either TiO₂ or Fe₂O₃, and varying amounts of Li₂CO₃ as a flux. The mixture is then pressed at 2,000 to 2,600 psi in a 1/2-in. mold.

(3) The material is brought into solution and the solution is sparked either directly or after being allowed to soak into a graphite rod. Feldman⁷ used a porous graphite cup with a thin base through which the solution passes; a panel⁸ of the British Non-ferrous Metals Research Association has described a copper cup method for sparking the solution directly, and Harvey⁹ used a rotating graphite disc, its lower edge dipping into the liquid and a spark passing between its upper edge and a graphite counter.

Muir and Ambrose¹⁰ use a cupped graphite electrode which has been heated to about 900°C for a few minutes. After a 60-sec pre-spark, 0.05 ml of the solution is dropped into the cup and, after the solution has soaked in, a spark discharge is passed between the cupped and graphite counter electrode.

Methods Used

Qualitative Analysis. Although standard procedures of qualitative analysis can be applied to ceramic materials, care must be

* Abridged version of paper in *Trans. Brit. Cer. Soc.*, **57**, 218 (1958). By permission.

exercised in the method of excitation. These materials usually consist of elements of widely differing volatility and if, for example, a glaze containing ZrO_2 is arced in a cavity-type electrode, the more volatile elements may distil, leaving a molten bead rich in ZrO_2 in the crater. If this bead is not volatilized before the walls of the crater are all burnt away, the bead may drop or spurt from the electrode, with low or even negative results for the amount of zirconium in the sample. In our opinion it is advisable therefore when dealing with such materials to spread the finely divided material onto a flat-topped electrode; on arcing, the sample tends to form a large number of small beads which volatilize more readily than a single, larger, bead.

Brode¹¹ has described in detail a number of methods of identifying the elements present. The method we use is a development of the R.U. (raies ultimes) powder technique developed by the G.E.C. research laboratories. The R.U. powder base consists of a mixture of ZnO , MgO and CaO . The spectrum obtained from this powder is recorded in juxtaposition with those obtained from an Fe-arc and the unknown by means of a Hartmann diaphragm. With the aid of enlargements of the R.U. spectrum¹² shown in juxtaposition to an iron arc on which lines are identified, fairly rapid qualitative analysis can be made. In the method used in this laboratory a borosilicate glass containing some 25 elements commonly encountered in ceramic analysis is used. This glass burns more smoothly than the R.U. powder, producing very little background and practically no CN bands, which are suppressed by the sodium and boron. The enlargements were prepared by using the standard projector as an enlarger and mounting the photographs on the edge of a card on which line identities are recorded. No iron reference spectrum is required, since the line pattern is characteristic and can easily be lined up with the projected image of an unknown recorded in

juxtaposition with the trace-element glass, since both are enlarged to the same extent.

Quantitative Analysis. *Raw Materials.*

It is essential to obtain a series of accurately analyzed samples covering the range within which analyses are expected to fall. Such samples are not always available and the method used to prepare such standards is described. A quantity of the purest obtainable material is first well mixed and carefully analyzed. Four or five 10-g portions are weighed out into platinum dishes and varying quantities of a solution that contains the impurities being sought is run into each. The mixtures are then evaporated to dryness, with constant stirring, on a water bath. The residue is finally baked at 110°C and ground by means of an agate mortar and pestle. If, as in the case of Co_3O_4 and NiO , the amounts to be added are too large to be conveniently added as solution, the oxides are mixed together with a little water and milled in a small ball-mill. Substances which are soluble in water are milled dry.

The electrodes used throughout are J.M.2.B. 65 mm of pure graphite. Some of the samples are mixed with twice their weight of pure graphite before arcing in an undercut cavity electrode while others are loaded into the cavity with no admixture. Both types of specimen are covered with a thin layer of graphite before the arc is struck. With samples of sand and quartz the finely ground material is spread on a flat-topped electrode. An 8-mm electrode gap is used for all D.C. work (see Table 1).

Rutile has an exceptionally complex spectra and, although the iron content can be determined by the method already detailed, the Cr and V require a preliminary chemical separation owing to the close proximity of interfering Ti lines to the sensitive Cr and V lines.

One gram of the sample is mixed with 0.75 g of anhydrous Na_2CO_3 and 0.05 g of NaF. These constituents are ground together by means of an agate pestle and mortar, and

TABLE 1. SUMMARY OF RAW MATERIAL METHODS

	Material	Slit width (mm)	Lines used	Remarks
Materials mixed with graphite in the ratio 1 sample: 2 graphite	Alumina	0.02	Al (control) 3066 Si 2881 Fe 3020 Cu 3274	The hydrated material must be ignited before use
	Calcspars	0.02	Ca (control) 3180 Fe 3020 Mg 2802 Cu 3274 Cr 4254	The arc is likely to be a little erratic
	Cobalt oxide	0.02	Co (control) 3098 Fe 3020 Ni 3101	
	Copper oxide	0.02	Cu (control) 3012 Fe 3020	
	Fluorspar	0.01	Ca (control) 3180 Si 2881 Fe 3020 Pb 2614 Mn 2798 Cu 3247 Al 3092	Light emission is very intense, hence the use of 0.01 slit. CaCO_3 , which is also an impurity in this substance, is estimated chemically
	Manganese dioxide	0.02	Mn (control) 3022 Fe 3020	
	Nickel oxide	0.02	Ni (control) 3032 Fe 3020 Co 3044	
	Titanium oxide	0.02	Ti (control) 3231 Fe 3020	Exposure 30-40 sec. For Cr and V see under solution methods
Materials not mixed with graphite	Antimony	0.02	Sb (control) 2850 As 2349 Pb 2614 Fe 3020 Cu 3274	Exposure 25-35 sec. Sample melts on arcing but burns well
	Barium carbonate	0.02	Ba (control) 3262 Fe 3020 Cu 3274	
	Zinc oxide	0.02	Zn (control) 3018 Pb 2614 Fe 3020 Cu 3273	This substance is likely to splutter a little until the arc is established
Material arced on a flat-topped electrode	Sand and quartz (ground fine)	0.02	Si (control) 2532 Fe 3020 Al 3092 Cu 3274 Cr 4254	

then sintered at dull red heat in a closed platinum crucible. The cake, which can easily be broken down with a glass rod, is leached with 30 ml of boiling water, the Ti remaining insoluble while the Cr and V pass into solution. The solution is then acidified with HNO_3 and 10 ml of a solution of $\text{Cu}(\text{NO}_3)_2$ containing the equivalent of 50 g CuO per liter is added. The total bulk is then made up to 50 ml in a graduated flask.

A 6.5 mm $\times$ 30 cm J.M.2.B. graphite rod is cut up into $\frac{3}{4}$ -in. lengths and the ends are filed square with a sharp file. These electrodes are then placed in a closed platinum vessel and heated at $1,000^\circ\text{C}$ for 20 min. An electrode, so prepared, is mounted in a small vice set in the de Gramont spark stand and a flat counter electrode is set 4 mm away. A simple condensed spark is run for 20 sec, after which 0.05 ml of the solution is dropped onto the surface. The solution takes about 60 sec to soak in, after which the spark is run for 60 sec. Cu 2961 is used as the control line; Cr 4254 and V 3184 are used as analysis lines.

Frits and Glazes. The solution method described above is used for the determination of major constituents in frits, glazes, etc. The main difficulty is in finding a suitable method of bringing the substance into solution. The best method we have found is to mix 1 part of sample with 5 parts of Na_2CO_3 and 5 parts of $\text{Na}_2\text{B}_4\text{O}_7$ and fuse in a platinum crucible at $1,000^\circ\text{C}$ for a time that depends on the composition. Enamel frits fuse fairly readily, whereas high-alumina clays and refractories require about 30 min. The melt is shattered by rapid cooling and dissolved in 30% v/v HNO_3 at room temperature. Under these conditions neither SiO_2 nor Sb_2O_3 is precipitated, but if much TiO_2 is present it must be complexed by the addition of 5 ml 20 vol. H_2O_2 with the acid. The 10 ml of copper internal standard is then added and the bulk is brought to 50 ml. The procedure is then exactly the same

as that described under the analysis of rutile.¹⁷

Fluorine. The excitation potential of the lowest energy line is very high and in consequence the spectrographer cannot readily make use of the atom lines of this element for analysis. In 1926, however, Ryde and Yates suggested the use of a CaF band for the determination of fluorine and the band head at 5291 is most often used. The excitation potential of CaF 5291 is very low, and its emission is only observed in the early stages of the discharge. An excess of Ca must be present and even if the sample contains Ca it is advisable to add a further quantity. Hughes¹⁸ used electrodes steeped in a saturated solution of CaCl_2 , but most workers mix the sample with CaCO_3 and graphite before loading the electrodes; this ensures that a large excess of Ca atoms is available at the commencement of the discharge, otherwise the very volatile fluorine may escape before the CaF molecule is formed.¹⁴

The standards for this work were prepared by melting five glasses in a small gas-fired pot furnace. Fluorine is lost during the melting process and careful chemical analyses were made of each.

The glasses were ground in agate to pass a 200-mesh sieve and 1 part of glass, 1 part of CaCO_3 and 4 parts of graphite were mixed by grinding together, before being loaded into the electrode cavity. In order to determine the exposure period, a curve of intensity against time was plotted. Approximately 15 mg of the mixture is arced and, 75% of the fluorine is evolved in the first 25–30 sec and all has been volatilized by 70 sec. Immediately after the fluorine has volatilized, background, probably due to CaO emission, becomes intense and it is inadvisable to prolong the exposure; in this work the exposure was for 75 seconds. If no very great variations in the Ca content of the samples are encountered, it is possible to use a Ca line as internal standard. Ca 5265 was used with success but in samples

where the Ca content varied, no suitable internal standard could be found.

Accuracy

Much has been written on the accuracy to be expected with spectrographic methods of analysis,¹⁵ and workers in this field differ as to what percentage deviation constitutes a quantitative and what constitutes a semi-quantitative analysis. Extensive work has not been carried out on the accuracy of the methods described, but from the results of replicate analysis and periodic chemical checks it can be stated that with the raw material control analyses using D.C. arc excitations a deviation, at best, of ± 10 – 15% of the amount of an impurity present can be expected. In the case of the solution-spark technique the deviation is about $\pm 4\%$ for all the elements determined except SiO_2 , for which a deviation of approximately $\pm 6\%$ was found.

Since the impurities in ceramic raw materials rarely exceed 1% and are mostly less than 0.5% , the accuracy of the D.C. arc methods described are adequate. Whether the determination of major constituents by the solution method is sufficiently accurate will depend on the requirements, but for most work it is adequate for constituents not exceeding 20% . However, the results obtained for constituents present even up to 70% may be of great value when time is short.

From time to time considerable deviations occur in single analyses, which can be attributed to bad sampling. Since the size of sample actually consumed in the discharge is small, great care must be exercised in sampling.¹⁶ It is advisable in all cases to carry out the determinations at least in triplicate, using separate samples if possible.

REFERENCES

1. AHRENS, L. H., "Spectrochemical Analysis" (Addison-Wesley, 1950).
2. KVALHEIM, A., *J. Opt. Soc. Amer.*, **37**, 585 (1947).

3. JAYCOX, E. K., *J. Opt. Soc. Amer.*, **37**, 162 (1947).
4. FITZ, E. J., AND MURRAY, W. M., *Ind. Eng. Chem. Anal. Ed.*, **17**, 145–147, 1945.
5. ANTHONY, J. W., CHANDLER, R. J., HUCKABOY, W. B., AND KENNER, C. T., *Analyt. Chem.*, **28**, 470 (1956).
6. ZANDER, J. M., AND TERRY, J. M., *J. Amer. Ceram. Soc.*, **30**, 366, 1947.
7. FELDMAN, C., *Anal. Chem.*, **21**, 1041 (1949).
8. British Non-ferrous Metals Research Association, Solution Methods Panel—R.35 Committee, *Metallurgia*, **44**, 45 (1951).
9. HARVEY, C. E., "Spectrochemical Procedures" (Applied Research Lab., Glendale, Calif., 1950).
10. MUIR, S., AND AMBROSE, A. D., *Spectrochim. Acta*, **4**, 482 (1952).
11. BRODE, W., "Chemical Spectroscopy" (Wiley, New York, 1956), Chapter 4.
12. Set of 7 enlarged photographs of the spectrogram (prism dispersion) of a sample of R. U. powder. Published by Hilger and Watts Limited
13. HUGHES, M., A.S.T.M. Special Tech. Pub. Nos. 76, 77.
14. AHRENS, L. H., "Spectrochemical Analysis" (Addison-Wesley, 1950). Chapter 14.
15. AHRENS, L. H., "Quantitative Spectrochemical Analysis of Silicate" (Pergamon, 1954), Chapter 4.
16. MELLOR, J. W., AND THOMPSON, H. V., "A Treatise on Quantitative Inorganic Analysis" (Griffin, 1938), Chapter 8.
17. ARGYLE, A., British Cast Iron Research Association. "Solution Method for the Spectrographic Analysis of Slags." (Private communication).

J. F. BROWN

COMPLEX SPECTRA*

The extension of the concepts and rules, developed for one-electron spectra, to include those originating in atomic configurations having more than one electron is fairly straightforward. The designation *complex spectra* emphasizes both the less obvious character of the regularities and the generally higher population density of spectral

* The fifth in a consecutively developed series of articles on the fundamentals of Optical Emission Spectra: see *Introduction: Designation and Description of Spectra* for list of topics, p. 202.

lines. Some authors prefer to subdivide these widely varying spectral types into several categories, including the fairly simple triplet-series spectra originating in two-electron configurations, such as those of zinc, cadmium and mercury, the moderately complex multiplet-pattern spectra of the long periods, and the extremely complex and densely populated spectra of the rare earths.

The conventional treatment of the ordinary features of complex spectra follows the Hund theory, and the vector model first used by Landé. Hund was the first to account for the energy levels by the combined effect of the valence electrons. According to the vector model, the various angular momenta are treated as vectors and combined according to a coupling scheme. The coupling scheme operating in the instance of spectra having the most regular intervals and intensities in multiple features, and the only one to be discussed in this article, is Russell-Saunders, or LS coupling. In the modern treatment each electron is characterized by an orbital angular momentum l and a spin angular momentum s . According to the LS -coupling scheme, the l -vectors are coupled together to form a resultant L , and the s vectors are coupled to form a resultant S . These resultants combine vectorially to form the resultant J . Physically this means that the interactions between the l -values and the interactions between the s -values are very much stronger than the respective magnetic spin-orbit interactions of the type l_s . The resultant L or total orbital angular momentum determines the character of the spectral term, following a scheme analogous to the one listed for doublet terms of one-electron spectra.

L -value 0 1 2 3 4 ...

Term S P D F G ...

The resultant S determines the multiplicity, which is always equal to $2S + 1$. Attention is called to an ambiguity in the notation re-

quiring a distinction to be drawn between the vector resultant, S , and the designation S -term, the latter being a term of L -value zero. The individual s -values, it will be remembered, are always equal to $\frac{1}{2}$. The structure of the multiple term may be understood when we note the possibilities associated with the vector combination of L and S to yield the total angular momentum J .

Suppose we consider the two-electron case. The s -values may combine to form a resultant 0, or 1. $S = 0$ corresponds to a singlet because its combination with L produces no effect. When $S = 1$, we have a triplet because the possible vector combinations are $L + 1$, $L + 0$, and $L - 1$. These possibilities are shown in the accompanying vector diagram for a selected type term.

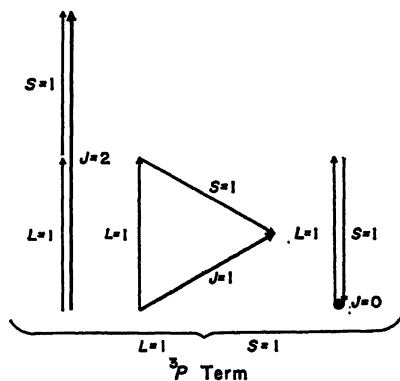


FIG. 1. Vector diagram illustrating development of multiple levels for a ^3P term.

The multiplicities associated with the S -values are as follows:

S	0	$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3 ...
Multiplicity	1	2	3	4	5	6	7

The multiplicity is always specified according to the S -value, but is not always realized. Thus an S -term, that is one of L -value zero, is always single. An actual five-fold term is only reached for D -terms and those of greater L value. A quintet P -term has only three possible levels with J -values 1, 2, 3. The possible J -values for a given L

and S may be written down readily by remembering that J can take all possible values in steps of one from the difference to the sum of L and S . Complete tables of possible multiplicities for n electrons and J -values of multiplets are to be found in the "American Institute of Physics Handbook."¹ It is to be noted that the highest multiplicity that can be realized is 11.

It might be expected that it would be possible to predict all possible terms for any configuration of valence electrons with known l -values. The Pauli exclusion principle sets up a limitation of this possibility when the configuration includes equivalent electrons, that is those of the same n - and l -values. In addition to the three quantum numbers, n , l , and s , associated with an electron, the quantum theory requires two others, the magnetic quantum numbers m_l and m_s . These are thought of as the quantized projections of l and s on the magnetic axis when a field so intense is applied to the atom that all couplings are broken and the vectors l and s precess independently about the axis. The Pauli principle states that precisely the same sets of quantum numbers cannot be duplicated in a given atom. By tabulating the possible sets of m_s and m_l for a given configuration of equivalent electrons, it is possible to arrive at the resultant values M_s and M_L and thus sort out the possible resultant S and L values to predict allowed terms. These procedures are outlined and illustrated by Hund and by White.² To give an example, a p^2 configuration would be expected to yield singlet and triplet S , P , and D terms (^1S ^1P ^1D ^3S ^3P ^3D). Applying the Pauli principle, only ^1S , ^1D , and ^3P are found to be possible. Complete tabulations of spectral terms arising from equivalent s , p , d , or f electrons are given by White² and in the "American Institute of Physics Handbook."¹ An important fact to be noted in these tables is that the array of terms for a given configuration of equivalent electrons is the same as that for a completed

shell of the same class of electrons less the given number. For instance, six p -electrons form a complete shell. Both p^2 and p^4 lead to the same set of terms ^1S , ^1D , ^3P . There is an important difference, however. In general, the j -values for the multiple terms arising from configurations comprising less than half of the electrons in the shell are regular, that is, terms with smaller j -values are lower, whereas terms from configurations comprising more than half, such as p^4 or p^5 , are usually inverted.

In the practical application of the vector addition scheme, to arrive at the number and characterization of the terms, there is a slight modification that generally applies when the configuration is partly composed of nonequivalent electrons. A kind of synthesis is envisioned according to which the electron configuration of an atom or ion is built up by the addition of an electron to one of the possible configurations of the next higher stage of ionization. These higher ion configurations, of course, account for the various terms of the next spectrum. The terms of the spectrum under consideration result from the addition of the s - and l -vectors of the added electron to the resultant vectors designated S' and L' , of the term of the higher spectrum. According to the coupling scheme s combines with S' to form a resultant S , and l combines with L' to form a resultant L . L and S combine, of course, to form the final resultant J , characterizing the levels of the new term. The term of the ion spectrum, characterized by L' and S' , is said to be the parent of the term obtained by adding the l - and s -vectors of the electron completing the configuration. The group of levels arising from the addition of an electron (not necessarily restricted to a single l -value) to the configuration of a given parent term is called a family. Permitted transitions between members of a family of terms are more intense than others. To illustrate the origin and lineage of terms in a typical spectrum, a table of predicted terms of Cl I is introduced

EMISSION SPECTROSCOPY—LIGHT

as an example. (This is a reproduction of Table 17, Vol. I, "Atomic Energy Levels." ³)

with structure in the limits. For instance, most of the rare gas levels form series ap-

PREDICTED TERMS OF Cl I

Configuration 1s ² 2s ² 2p ⁶ +	Predicted terms				
3s ² 3p ⁴ 3s 3p ⁴			² P° ² S		
	ns(n ≥ 4)	np(n ≥ 4)	nd(n ≥ 3)	nf(n ≥ 4)	...
3s ² 3p ⁴ (² P)nx	$\begin{Bmatrix} ^4P \\ ^2P \end{Bmatrix}$	$\begin{Bmatrix} ^4S^{\circ} \ ^4P^{\circ} \ ^4D^{\circ} \\ ^2S^{\circ} \ ^2P^{\circ} \ ^2D^{\circ} \end{Bmatrix}$	$\begin{Bmatrix} ^4P \ ^4D \ ^4F \\ ^2P \ ^2D \ ^2F \end{Bmatrix}$	$\begin{Bmatrix} ^4D^{\circ} \ ^4F^{\circ} \ ^4G^{\circ} \\ ^2D^{\circ} \ ^2F^{\circ} \ ^2G^{\circ} \end{Bmatrix}$	...
3s ² 3p ⁴ (¹ D)nx'	² D	² P° ² D° ² F°	² S ² P ² D ² F ² G	² P° ² D° ² F° ² G° ² H°	...
3s ² 3p ⁴ (¹ S)nx''	² S	² P°	² D	² F°	...
3s3p ³ (² P°)nx'''	$\begin{Bmatrix} ^4P^{\circ} \\ ^2P^{\circ} \end{Bmatrix}$	$\begin{Bmatrix} ^4S \ ^4P \ ^4D \\ ^2S \ ^2P \ ^2D \end{Bmatrix}$	$\begin{Bmatrix} ^4P^{\circ} \ ^4D^{\circ} \ ^4F^{\circ} \\ ^2P^{\circ} \ ^2D^{\circ} \ ^2F^{\circ} \end{Bmatrix}$	$\begin{Bmatrix} ^4D \ ^4F \ ^4G \\ ^2D \ ^2F \ ^2G \end{Bmatrix}$	...

This leads to the presentation of the notation for the complete quantum description of a level. First is given the electron configuration of the ion, followed in parentheses by the designation of the parent term; this in turn by the designation of the added electron; and finally the resultant term with its *j*-subscript to distinguish the level. The following example selected from Cl I is a completely described multiplet. Computed values of wave numbers are shown in appropriate positions as level differences. Observed values are represented by incomplete numbers. Intensities are shown in parentheses.

proaching one or the other of the levels of the *p*⁵ ²P state of the ion. In the instance of xenon, these doublet limits are separated by more than 10,000 cm⁻¹.

When one examines spectra of elements in ascending or descending order of atomic numbers, there is an alternation of even and odd multiplicities, something that is to be expected since the multiplicity depends on the summation of the *s*-values of the electrons that contribute to the spectrum.

Iso-electronic spectra have been mentioned in connection with hydrogenic spectra such as H_I, He_{II}, Li_{III}, and so on. An atom of any element has the same external

3d + ³ P →		⁴ D _{3/2}	⁴ D _{5/2}	⁴ D _{1/2}	⁴ D _{0/2}
↓	4p + ³ P	17015.87	16915.22	16806.90	16722.65
		0.56(717)	1.13(227)	9.33(21)	
⁴ P° _{3/2}	22076.46	5060.59	5161.24	5269.56	
			9.30(227)	7.61(185)	1.76(6)
⁴ P° _{1/2}	21864.41		4949.19	5057.51	5141.76
				3.67(56)	7.81(85)
⁴ P° _{0/2}	21630.45			4823.55	4907.80

FIG. 2. Selected multiple line pattern in Cl I.

The various series in a spectrum approach different ion limits, according to the family in which the series-forming levels are grouped. The limiting term also conforms

electron configuration as that of the singly ionized atom of next higher atomic number, and therefore the same number of terms with the same set of quantum designation, al-

though different in actual magnitude. The same applies to the doubly ionized atom higher by two in the atomic number sequence, and so on. Iso-electronic sequences of spectra appear in this manner. Known examples are tabulated in "Atomic Energy Levels."⁸ Nearly all known spectra are bracketed in some iso-electronic sequence.

Selection rules governing transitions are not to be considered absolute, but rather the expression of a probability. The usual rules may not hold in the presence of perturbing influences such as strong electric or magnetic fields. Since there are many possibilities for resultant L arrived at by a summation of vectors, a rigid selection rule for ΔL is not expected and is not found in many-electron spectra. Usually, $\Delta L = 0$ or ± 1 , but transitions with $\Delta L = 2$ are not infrequent. The rule of parity is generally obeyed. Terms are said to be of even or odd parity if the arithmetical sum of the l -values of all the electrons is even or odd. Practically, this means that one needs only find the sum of the l 's for p and f -electrons. Transitions between terms of the same parity do not occur in the usual case of dipole radiation. In this situation it is assumed that the radiating field around an atom is approximately equivalent to the field of a vibrating electric dipole. For quadrupole radiation the opposite rule applies, namely, that transitions between terms of the same parity occur. Interesting examples are the coronal line, interpreted as the transition between the levels of the ground doublet of Fe XIV and a similar transition between the levels of the ground doublet of the first spectrum of iodine located at $\lambda 13,149\text{\AA}$. The ΔL -rule for doublet spectra contains the parity rule inherently. The selection rule for J is that $\Delta J = 0$ or ± 1 , the transition 0 to 0 being excluded.

The formal treatment of multiplet separations is an extension of that discussed for doublets in one-electron spectra. The value of the energy of interaction between the

spin and orbital magnetism in the one-electron case is given by $\gamma = a l^* s^* \cos(l^* s^*)$ which leads to the doublet separation if we find the difference in the values of γ for the two j -values. In the instance of Russell-Saunders coupling, all electronic spins s_i form a resultant S and all orbital momenta l_i form a resultant L , while S and L finally combine to give a resultant J . The total interaction between the spins and the respective orbits of the electrons is then:

$$\Gamma = \sum a_i l_i^* s_i^* \cos(\overline{l_i^* s_i^*})$$

the barred factor indicating an average. This leads to a result of the form

$$\begin{aligned} \Gamma &= AL^*S^* \cos L^*S^* \\ &= \frac{1}{2}A[J(J+1) - L(L+1) - S(S+1)] \end{aligned}$$

The latter form contains the interval rule of Landé. If we consider two successive levels of the same multiplet characterized by J and $J - 1$, we have

$$\Gamma(J) - \Gamma(J - 1) = A(J)$$

The subsequent intervals are thus proportional to the larger value of J corresponding to one of the two adjacent levels. Goudsmit⁴ derived formulas for the values of Γ or A in cases where only equivalent electrons were responsible for the term. It was possible to express A in terms of the values of a_i for the single electrons which, of course, are all equal. In a simultaneously published paper Goudsmit and Humphreys⁵ showed that it was possible to determine A for other configurations of electrons. In general, the method was to consider the addition of another electron to a group for which A is known, and to obtain a new A in terms of that of the original group and a_i of the new electron, or the expression for A , and consequently that for the total separation, may be in terms of a_i for the different electrons. Examples were displayed from iron and oxygen spectra.

It is expected that the theoretical scheme for describing complex spectra may be modi-

fied considerably as a result of a new treatment developed by Layzer⁶. According to this scheme, charge Z enters explicitly into all predictions of level positions. Spectral terms are no longer assigned to definite configurations, but rather to more comprehensive aggregates called complexes, and the notion of screening takes on a precise quantitative meaning.

REFERENCES

1. "Am. Inst. Physics Handbook," McGraw-Hill, New York, 1957.
2. H. E. WHITE, "Introduction to Atomic Spectra," McGraw-Hill, New York, 1934.
3. CHARLOTTE E. MOORE, "Atomic Energy Levels," Circular Nat. Bur. Standards 467, I (1949), II (1952), III (1958).
4. S. GOUDSMIT, *Phys. Rev.*, **81** (1928).
5. S. GOUDSMIT AND C. J. HUMPHREYS, *Phys. Rev.*, **31**, 960 (1928).
6. D. LAYZER, *Ann. Phys. (N.Y.)*, **8**, 271 (1959).

CURTIS J. HUMPHREYS

CURRENT STATUS OF EMISSION SPECTROSCOPY*

This topic, owing to the temporary validity of any summary, is probably most suitable for treatment in periodic review articles or progress reports. Nevertheless, it is deemed desirable to summarize briefly both what has been accomplished and what remains to be accomplished in the observation and analysis of spectra and to call attention to new developments in the state of the art that open up new areas of investigation and make the experimental approach vastly different from what it was in the period of maximum activity around 1930.

To set up a backdrop for the discussion, it is noted that a total of 102 elements has been discovered, counting a few artificially created ones, of which only trace amounts have been isolated. The number of possible spectra of these elements and their ions is

the sum of the series of consecutive numbers from 1 to 102, namely 5,253. "Atomic Energy States" by Bacher and Goudsmit,¹ published in 1932, reported energy level values for 231 spectra of 69 chemical elements. In 1939 Shenstone² published a rating of 400 analyzed spectra, using letters A to E to indicate the state of the analysis. This rating chart has been reviewed and revised periodically by Meggers^{3, 4} with the assistance of Dr. Charlotte Moore-Sitterly. The 1946 publication³ listed 378 articles covering the various spectra as providing the basis of the ratings. The most recent revision of the rating chart⁴ contains entries for 511 spectra of 87 elements, indicating that only about 10 per cent of all available spectra have been investigated in some degree.

Several of the recent additions to the list have been spectra of artificially produced radioactive elements. Particularly noteworthy among these is technetium, element 43, analyzed by Meggers and Scribner.^{5, 6} This element is especially interesting because, while not occurring naturally on the earth, it is present in certain types of red giant stars. As of 1959 the gaps in the list of analyzed spectra included elements of atomic number 61, 67, 68, 85, 87, 91, 94, 96, and higher, although experimental material had been obtained for all below 95 except 85, 87, and 91. The two groups of rare earth elements, comprising the 4f- and 5f-types respectively, are those for which there is the greatest scarcity of information, in some instances none at all. This dearth of material includes both experimental data and analyses. All the 5f-type rare earths of atomic number 93 and higher are artificially produced radioactive elements. Available techniques for handling such radioactive materials would probably permit observation of their spectra if sufficiently large samples could be prepared. Owing to the large number of levels associated with 4f- and 5f-configurations, spectra of the rare earth elements are necessarily densely populated and complex. The excitation potentials

* The ninth in a consecutively developed series of articles on the fundamentals of Optical Emission Spectra: see *Introduction: Designation and Description of Spectra* for list of topics, p. 202.

of the first spectra are low. Consequently it is difficult to devise and control sources to bring out these spectra without a preponderance of second and higher spectra.

It is expected that much of the observational material for the first spectra will be found in the infrared beyond the photographic limit. The highest precision of recording and measurement of these spectra will be required to permit discrimination between significant and fortuitous regularities. The enormous amount of material in a description of such a spectrum will make imperative the use of digital computers for reduction of data and energy-level search if reasonable progress is to be made. Zeeman-effect observations will probably be needed to make a correct assignment of quantum numbers to the levels. Compilation of the energy levels resulting from these analyses will complete the material for the final volume of "Atomic Energy Levels".

Zeeman-effect data where available are generally included in papers presenting energy-level analyses. No attempt is made here to estimate the number of spectra for which Zeeman-effect observations have been made. The literature references indexed in "Atomic Energy Levels" are coded to indicate the inclusion of such material. In many instances the observations could be improved by use of higher fields. Square-wave pulsing techniques now coming into use offer promise of achieving these high magnetic flux densities without the use of the bulky and cumbersome equipment heretofore required.

For the current accumulation of material on nuclear moments derived from hyperfine structure measurements, reference is again made to a recent publication by Meggers⁴ where it is pointed out that one or more nuclear moments are now known for all stable isotopes with odd mass numbers, excepting

Although the quality of direct interferometric optical observation of hyperfine structures is improving, owing in large measure to the impressive work of Jacquinet and his associates at the Bellevue Laboratory in France, more and more effort is going into various magnetic resonance experiments which were given great impetus by the well-known experiments of Lamb and Retherford⁷ in sorting out and interpreting the details of hydrogen fine structure.

Probably one of the most neglected areas related to observation and description of spectra is that of quantitative intensity measurements. The intensity notations included in published descriptions are in most instances merely visual estimates noted during comparator measurements. Precise measurements have been tedious and difficult owing to the complicated procedures of plate calibration. Present-day radiometric scanning methods are extremely promising when one considers speed, simplicity, and reliability. Items to be considered are direct presentation of line profiles and attainable linearity of both detectors and amplifiers within certain limits, or, under less favorable circumstances, knowledge of the characteristics of these devices.

Availability of fast, high-response detectors has brought a new dimension to spectroscopy by making high-resolution grating techniques possible for observations in the infrared region. Although relatively few atomic emission lines intense enough for observation are found beyond 30,000 Å, there is no longer any physical barrier limiting observation such as was formerly set by the upper wavelength limit of photographic response near 13,000 Å. The equipment consists of a mirror-grating spectrometer arranged for scanning the energy pattern emerging from the exit slit. A lead sulfide or other lead salt photoconductor is commonly used as the detector, its output being amplified and fed to a commercial potentiometer-recorder. Although extensively used for investigating the rotational structure of

$$\frac{57}{28} \text{ Fe}, \frac{61}{28} \text{ Ni}, \frac{161}{66} \text{ Dy}, \frac{163}{66} \text{ Dy}, \text{ and } \frac{187}{76} \text{ Os}.$$

molecular bands, such equipment has found relatively little employment in the study of atomic spectra. A survey of such work is contained in two reports by this author,^{8, 9} the second in collaboration with E. Paul, Jr.

No up-to-date treatment of any aspect of electromagnetic radiation can be completed properly without some reference to space technology. Up until the very development of space probes, along with which we shall group for purposes of this discussion high-altitude flights of balloons and aircraft, carrying spectrographic equipment, any spectroscopic examination of extraterrestrial light-emitting sources was completely cut off by ozone absorption in the ultraviolet beginning at about 2900 Å and extending to shorter wavelengths. This entire region is now opened up as a result of new data being obtained from spectrographs carried above the denser portion of the atmosphere by rockets or manned aircraft. These devices are especially important for solar research. Balloon platforms are considered practical for astrophysical observation because the improved performance of light-gathering optics in the absence of dense atmosphere permits a significant reduction in the size of the components.

The import of these developments for laboratory experimentation is that more controlled experiments with known source materials and with similar spectral coverage will be required to interpret data obtained from previously inaccessible sources. In many instances, the sensitive lines required to establish identification of atoms or ions previously unidentified in the sun or stars are located in the extreme ultraviolet. Emission spectroscopy in the Schumann region comparatively inactive since the period associated with the work of Millikan and Bowen is receiving increased emphasis because of the data accumulating from extra-atmospheric observations.

REFERENCES

1. R. F. BACHER AND S. A. GOUDSMIT, "Atomic Energy States," McGraw-Hill Book Co., New York (1932).
2. A. G. SHENSTONE, "Reports on Progress in Physics," University Press, Cambridge, Vol. 5, p. 210 (1939).
3. WILLIAM F. MEGGERS, *J. Opt. Soc. Am.*, **36**, 431 (1946).
4. WILLIAM F. MEGGERS, "Revue Universelle des Mines," 9th Series, **15**, 230 (1959).
5. W. F. MEGGERS AND B. F. SCRIBNER, *J. Research N.B.S.*, **45**, 476 (1950).
6. W. F. MEGGERS, *J. Research N.B.S.*, **47**, 7 (1951).
7. WILLIS E. LAMB, JR. AND ROBERT C. RETHERFORD, *Phys. Rev.*, **72**, 241 (1947).
8. CURTIS J. HUMPHREYS, NOL-Corona Report 146, U.S. Naval Ordnance Laboratory, Corona, California (1954). *Lunds Universitets Årsskrift* Avd. 2. Bd 50, Nr 21 (1954).
9. C. J. HUMPHREYS AND E. PAUL, JR., NAVORD Report 4589, NOLC Report 341, U. S. Naval Ordnance Laboratory, Corona, California, (1956).

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DETONATION-TEMPERATURE MEASUREMENTS

The temperature in the detonation zone of solid and liquid explosives may be measured by a two-color method in which the quality of the emitted radiation is evaluated by a multiplier phototube color pyrometer. The novel aspect of the technique employed is in the means of radiation sampling. A cylindrical polymethyl methacrylate probe, introduced into the explosive charge during fabrication, "pipes" the radiation from within the charge into the optical system of the sensing equipment. Since the rod probe extends axially into the end of the charge, the radiation source is from a zone of high confinement and should be characteristic of the "infinite" slab and representative of steady-state conditions within the charge near the core. Also, an important consequence of this technique is the radiation burst which persists for several microseconds during the passage time of the detonation zone along the rod; this reduces the response

requirements of the electronic recording system to practical limits.

The method used for measuring detonation temperatures is based on the energy distribution of the radiation emitted from the detonating explosive. According to Wien's law, the energy radiated by a black-body at temperature T at any wavelength λ in a band of width $\Delta\lambda$ is

$$E_\lambda = c_1 \lambda^{-5} e^{-c_2/\lambda T \Delta\lambda} \quad (1)$$

However, if two channels are employed, it is unnecessary to measure absolute energies since a ratio will suffice; thus,

$$\ln \frac{E_1}{E_2} = -5 \ln \frac{\lambda_1}{\lambda_2} - \frac{c_2}{T} \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right) + \ln \frac{\Delta\lambda_1}{\Delta\lambda_2} \quad (2)$$

Equation (2) may be converted to common logarithms and written in the form

$$\log (E_1/E_2) = A + B(1/T). \quad (3)$$

Here constant B is a function of the wavelengths used and can be found from the constants of the apparatus, while constant A may be determined by measuring ratio E_1/E_2 of a black or gray body at a known temperature.

In practice, neither the absolute energies nor their ratio is determined directly. Instead, the radiation of a particular wavelength falls on a multiplier-type phototube, and the voltage developed across its load resistor is measured by a cathode-ray oscillograph. The deflection of the cathode-ray oscillograph beam is then proportional to E ,

$$D = kE \quad (4)$$

Replacing E in (3) with D/k yields

$$\log (D_1/D_2) = \log (k_1/k_2) + A + B(1/T) \quad (5)$$

and combining constants

$$\log (D_1/D_2) = A' + B(1/T). \quad (6)$$

Equation (6) is used to calibrate the apparatus and to determine the temperature of detonation.

The components of a charge include the plastic rod with an opaque end, the sur-

rounding charge, two booster pellets of identical density and material, the oscillograph sweep synchronizing station, a tetryl booster, a detonating fuse, and the support stand and container. The rod probe is introduced into pelleted-type charges, for loading densities above 1.2 g/cm³, at the time of fabrication with a tableting machine; this results in a close fit between the rod and the explosive material. Charges under 1.2 g/cm³ are hand-packed into 1-inch-inner-diameter rigid plastic tubes having a wall thickness of 1/8 inch. Rods for both type charges are machined from cast slabs of "Plexiglas" UVA II stock. All rods used are 6 mm in diameter and extend about 2 cm into the charge. The inner end of the rods are machined to a cone to permit explosive powder flow around the rod end during filling and pressing. Maximum densities will be limited to about 1.58 g/cm³ since the use of greater pressures required for the higher densities results in pellet cracking. The conical rod end is coated with opaque black lacquer to limit radiation pickup during the passage of the detonation zone over the rod end. This is necessary since the optical transmission with end-on pickup is apparently much greater than with side pickup. Omission of an opaque coating causes serious overload of the electronic circuits.

It is necessary to vacuum-impregnate the granular charges with, and fire them in, a gas having a low ratio of specific heats (γ); otherwise apparent temperatures obtained from low-density charges in which the impregnation is omitted will be high (compared to impregnated charges) by a factor of two or three. All charges are identically processed by three cycles of evacuation and impregnation with propane. The charge is placed in a cellulose acetate container which maintains the ambient atmosphere of propane in and around the charge during firing. Impregnation, storage and handling are facilitated by the use of glass desiccators.

EMISSION SPECTROSCOPY—LIGHT

An ionic conduction probe is introduced into the charge to provide synchronization of the oscillograph sweep to the detonation. An opaque paper baffle and sleeve are placed over the portion of the rod which protrudes from the charge to prevent admission of unwanted luminous background radiation into the system.

An image of the plastic rod end is focused on a modified entrance aperture of a 21-foot Jarrell-Ash spectrograph. The entrance slit is replaced by a circular hole about 2 mm in diameter which admits the radiation from the entire rod end. A 15,000-line/inch concave grating is used, giving a dispersion of 5 Å/mm. The spectrograph is modified further by replacing the photographic plate holder with a multiple exit-aperture plate. The exit apertures are positioned so that the entire photographic plate width is used to provide maximum physical separation for four channels. A DuMont Type 6292 multiplier phototube is placed behind each of the exit slits; tubes are selected to provide maximum response for the wavelengths employed. The receivers are placed about 600Å apart and are centered on the following center frequencies for each wavelength band of approximately 100Å width: 6081Å, 5461Å, 4843Å, and 4223Å. The 5461Å channel is used as the reference for the accurate adjust-

ment of the plate holder position. All tubes are optically and magnetically shielded. The output of each phototube is coupled through a cathode follower and a low-impedance line to a wide-band, high-gain cathode-ray oscilloscope. The over-all frequency response of the electronic system is uniform to about 10 Mc with a linear vertical deflection of 6 cm. Oscillograph traces are recorded photographically with Du Mont-Polaroid cameras having $f/1.9$ lenses and using either Pola-Pan 400 film or Eastman Royal-Pan film.

Dynamic calibration of the apparatus is made before each test. Temperature calibration consists of admitting radiation from the target of a radio-frequency excited lamp of known temperature and emissivity into the system. The lamp consists of a $\frac{5}{16}$ -inch tantalum carbide disk supported in a water-cooled field concentrator by a zirconium oxide rod; this assembly is contained in an argon-filled glass envelope at a pressure of 2 atmos. The lamp is placed in the water-cooled work coil of a 1.5-kw radio-frequency generator operating at approximately 3.5 Mc. An image of the radiation source is formed on the spectrograph entrance aperture so that only radiation from the temperature-gradient-free center zone passes into the spectrograph. A motor-driven light chopper, having a narrow slit in the periph-

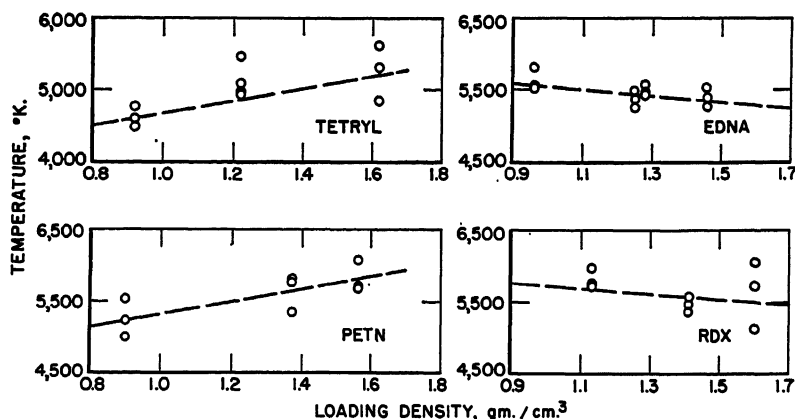


FIG. 1. Temperature-density relationship for four pure-compound explosives where each point is the average of six two-channel combinations for a single test.

ery, interrupts the radiation into approximately 50- μ sec pulses, and a photoelectric synchronizer permits the sweep to be triggered before each pulse.

Since the slope of the calibration is established by the wavelength bands for each color pair combination, only the intercept needs to be experimentally established. For this purpose, the lamp is operated in the region of 2800°K; checks are made on the

TABLE 1. TEMPERATURES OF DETONATION AS DETERMINED BY AN ELECTRO-OPTICAL METHOD

The temperature reported for each test represents the average of six temperatures obtained by the six possible pair combinations when using four wavelengths. All charges were propane impregnated.

Density, g/cm ³	Temperature, °K	Density, g/cm ³	Temperature, °K	
PETN		RDX		
0.90	5525	1.13	5715	
	5225		5970	
	5000		5742	
1.37	5762	1.41	5367	
	5756		5462	
	5343		5577	
1.56	6079	1.60	6056	
	5684		5734	
	5705		5136	
TETRYL		EDNA		
0.92	4479	0.96	5819	
	4750		5525	
	4600		5547	
1.22	5464	1.25	5241	
	4975		5368	
	4940		5485	
	5093	1.28	5437	
1.62	5619		5430	
	4837		5585	
	5297	1.46	5526	
			5263	
			5375	
		NITROGLYCERIN		
		1.60	3896	
			4095	
			4079	

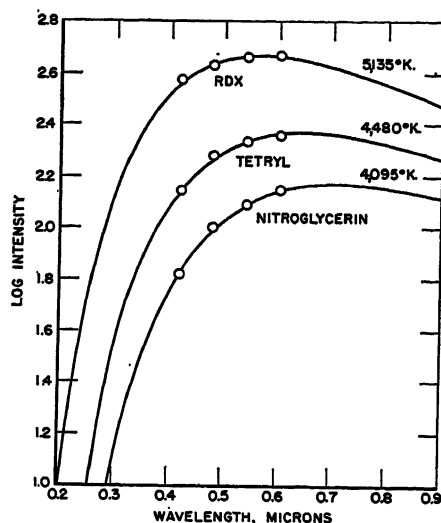


FIG. 2. Radiation distribution curves for a liquid (nitroglycerin), a low-density granular (0.92 g/cm³ tetryl), and a high-density granular (1.60 g/cm³ RDX) explosive. A black-body curve is constructed through the reference intensity level at 0.55 μ for each explosive test.

fit of four calibration lamp temperatures (2770°K, 2640°K, 2480°K, and 2310°K) for the six channel combinations.

The rf lamp temperatures are determined during the calibration period with a disappearing-filament type optical pyrometer and converted to the true temperature by application of an emissivity for tungsten carbide of 0.55 at a wavelength of 6600Å and a temperature of 2500°C.

Observed detonation temperatures vs. loading density obtained with the spectrographic method for PETN, tetryl, RDX, and EDNA are shown graphically in Figure 1 and given in Table 1 where each temperature is the average of six temperatures obtained from the six possible pair combinations using four wavelength channels. Table 1 also gives the detonation temperature of nitroglycerin viewed end-on, without rods. The average deviation from the mean for each explosive material is 180°K for PETN; 180°K for tetryl; 173°K for RDX; 92°K for EDNA; and 85°K for nitroglycerin.

The radiation-energy distribution relative to the energy of the 5461A channel for tests on RDX (1.60 g/cm³), tetryl (0.92 g/cm³), and nitroglycerin are shown graphically in Figure 2. A black-body curve is constructed through the reference channel and the experimentally determined points are plotted; good distribution agreement is shown. The data on the granular materials were obtained by the probe method, and the data on the liquid explosive were accumulated without probes by looking into the charge end-on through the undetonated transparent explosive. It was established that the rods had little effect upon the temperature measurement by tests with nitroglycerin with and without rods; the standard deviation was 10°K.

The detonation temperature of nitroglycerin was found to be 4000°K for high-order detonation (verified by velocities of about 7500 m/sec obtained from the radiation-time characteristics of the temperature oscillograms). Initiation of nitroglycerin by weak mercury fulminate-potassium chlorate detonators produced temperatures of approximately 3200°K for the low-detonation-velocity regime of 1500 to 2000 m/sec.

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M. L. BOWSER,
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DIRECT-READING MEASUREMENTS

The measurement of intensities or relative intensities by photographic procedures is time-consuming, requires calibration of the emulsion, and has an accuracy at best of between 2 and 3%. Direct photoelectric measurements of intensity are linear, rapid and accurate to 0.5 to 1% for a steady source. Direct photoelectric measurement of spectra by now would largely have replaced photographic procedures were it not for the expense and the inflexibility of such measurements. At least five different basic methods of direct measurements have been de-

scribed, as follows:

(1) Scanning continuously through the spectrum, recording the intensity as a function of wavelength. It must be realized that time is an implicit variable. The trace has no significance unless the characteristics of the source remain strictly constant with time.

(2) Stepwise scanning, i.e., moving rapidly to a line of interest and then scanning across it slowly. Again the source must remain constant.

(3) Sequential reading of line intensity with time: the exit slit stays centered on the line but the intensity is recorded as a function of time.

(4) Simultaneous integration of the intensity of all lines of interest over an exposure period usually of 10 to 100 seconds.

(5) Sequential integration: integrating of the intensity of an analytical line with respect to a reference line for 10 to 20 seconds, then moving the analytical exit slit to another analytical line and repeating the process.

The following description amplifies each method and comments on its advantages and disadvantages.

Scanning the Spectrum

Direct scanning spectrometers suitable for recording emission lines have been built by Leeds and Northrup and by Jarrell-Ash Company, according to the Ebert design of Fastie¹ (see page 180). The ARL 1.5 Meter and Jarrell-Ash 3.4 Meter Spectrographs may be converted to scanning spectrometers.

A scanning spectrometer is the least expensive means for measuring the relative intensities of a series of lines, since a single exit slit, photodetector and electronic circuit suffice, and the mechanical drive need not be complex. The resolution achievable is equivalent to that of the photographic plate, far superior to other direct-reading procedures. However, the method is suitable for

accurate quantitative measurements only if the source remains completely stable with time. Such is indeed the case for many flames, and for hollow-cathode, high-frequency and metallic vapor discharge lamps.

Broida has described procedures for analyzing hydrogen and deuterium mixtures in the presence of air², N^{15}/N^{14} isotope ratios³ in nitric acid or nitrogen, and C_{13}/C_{12} isotope ratios in flames⁴, using a scanning spectrometer and discharge tubes. In flame photometry, scanning spectrometers are now frequently used to measure the intensity of emission lines with respect to background. The height of the line above background is relatively independent of interelement effects and the better spectral purity achieves higher sensitivity than is possible with filter photometers.

In applied spectrochemical analysis, efforts to use a scanning spectrometer technique have been disappointing. Even in a spark, where fractional distillation effects are minimal, successive exposures of the same sample may not give sufficiently reproducible intensity ratios, even when the instrument is programmed to read specific line pairs after the same elapsed time. When, in a series of samples, several elements vary independently, the problem of achieving sufficient accuracy becomes still greater.

A typical electronic circuit for such a scanning spectrometer will consist of: (a) a power supply, adjustable to give 500–1200 volts (for nine-stage photomultipliers), or 500–2000 volts (for thirteen stages), regulated to $\pm 1\%$ for input fluctuations of $\pm 5\%$, with drift not greater than $.1\%$ per hour; (b) a sensitive DC amplifier, with high feedback for stability, a wide range of gain settings, a background suppression adjustment and a short response time (less than 1 second); and (c) a strip chart recorder. The over-all sensitivity may be capable of giving full scale response for a photomultiplier output of 10^{-8} to 10^{-9} ampere.

Stepwise Scanning. Several investiga-

tors (Wolfe and Enns, Menzies) have attempted to develop a direct-reading procedure in which the spectrometer moves rapidly to an analytical line, scans slowly across it, then moves rapidly to the next line, scans slowly across it, and so on. A strip chart recorder indicates the relative intensities of the analytical line and a section of the undispersed radiation isolated by a filter. Although the arrangement has the advantage of high optical resolution and exact centration of the exit slit is not necessary, it has been found impossible so far to maintain sufficiently constant or reproducible conditions of sample excitation, and adequate accuracy has not been achieved.

Scanning in Time. Radio Cinema of Paris, in its "Spectrolecteur", has employed a system in which a slit and photomultiplier move successively and precisely from one analytical line to another. It is claimed that the slit can be centered on each line with a precision of one micron. At each stop, the intensity ratio of that particular line, with respect to the intensity of an internal standard line measured by a fixed exit slit and photomultiplier, is recorded as a function of time on a strip chart recorder. The time constant of the recording system is approximately 20", so that short-term variations do not record. In a typical scan, there may be a pre-spark period of 30" to stabilize the discharge, then a 20" record for a first element, a 5" interval required for the slit to set on the new line, a 20" record, and so on through the determination of all elements.

The method is capable of an analytical precision of 2–3% of the concentration measured. A complete analysis for ten elements may require five minutes. The electronic system is simpler and less expensive than in integrating direct readers, but this advantage is largely offset by the expense of the mechanical workmanship required to achieve the necessary precision of slit setting.

The Spectrolecteur was the first direct reading spectrometer used extensively in Europe.

Integrating Direct-Reading Spectrometers

Experience has demonstrated that direct-reading measurements on sources which exhibit rather wide instantaneous variations in both over-all light levels and in line intensity ratios can nevertheless become surprisingly reproducible if the intensities of all lines are integrated simultaneously over periods of ten to sixty seconds. For this reason, integrating direct-reading instruments are more widely employed than scanning types, particularly for routine spectrochemical analysis. Indeed, all the really successful commercial instruments are of this type. For this reason, integrating direct readers are considered in some detail. The following discussion of spectrometer characteristics applies also to the scanning spectrometers previously discussed. Important features in the spectrometer (sometimes called a "polychromator") are as follows.

The Flux-Transmitting Power. The flux-transmitting power of the spectrometer depends on: The transmission or reflectance of the optical elements, the effective area and angular dispersive power of the dispersing element, and the ratio of slit height to focal length. Naturally, the greater the flux transmitting power, the stronger any given signal will be.

Entrance-Exit Slit Combinations. The signal-to-background ratio achieved depends

on the selection of entrance and exit slit widths.

The illumination at the focal plane of the spectrometer, for a spectral line, increases as the entrance slit is opened, only so long as the natural breadth of the spectral line in the source is less than the nominal slit width, plus any diffraction or aberration broadening. Once this slit width is exceeded, the illumination no longer increases, but the image broadens out. On the other hand, the illumination in the exit plane, for a continuous source (i.e., background), will increase linearly with entrance slit width, indefinitely. The consequences are illustrated by Figure 1 and Table 1.

Figure 1 shows the effect of different combinations of entrance and exit slit widths for a large spectrometer if we assume that the illumination of a spectral line in the exit slit plane for an 8 micron entrance slit can be represented approximately by a triangle with a 16 micron base. The line is broadened by diffraction and by aberrations. We assume an intensity of 24 (arbitrary units) for the line itself. As the entrance slit is opened, the illumination at the center of the image remains at 24 units above background and the image grows wider. The total flux for the line can be measured by the area of the triangle or trapezoid. The background illumination, which has been assumed to equal 1 on the same arbitrary scale for a slit width of 12.5μ , will be only .64 for the 8μ slit, and will increase to 2 for 25 microns, 4 for 50 microns, and 8 for 100 microns. The flux for the background is equal to the illumination times the slit width. (It is assumed that there is no nearby line to cause interference.) The resulting integrated flux for lines and background, and the ratio of the two, are recorded in Table 1. From this table we can draw the following conclusions:

(a) The signal to background ratio is inversely proportional to the width of the widest slit used, whether it be the entrance or exit slit.

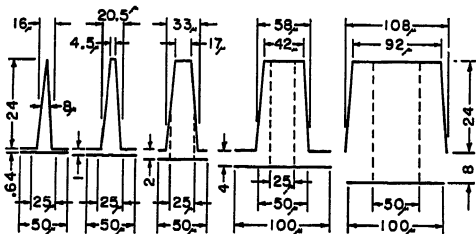


FIG. 1. Theoretical effect of entrance and exit slit widths on line to background ratio.

DIRECT-READING MEASUREMENTS

TABLE 1. EFFECT OF ENTRANCE AND EXIT SLITS ON LINE/BACKGROUND RATIO

Entrance Slit	8 μ	12.5 μ	25 μ	50 μ	100 μ
Line Intensity	24	24	24	24	24
Background Intensity	.64	1	2	4	8
Exit Slit					
25 μ					
Line Flux	$\frac{1}{2}(16)24 = 192$	$\frac{1}{2}(4.5 + 20.5)24 = 300$	$\frac{1}{2}(17 + 33)24 = 552 - \frac{1}{2}(8)12$	$25 \times 24 = 600$	600
Background Flux	16	25	$2 \times 25 = 50$	100	200
Ratio	12:1	12:1	11:1	6:1	3:1
50 μ					
Line Flux	192	300	600	1152	1200
Background Flux	32	50	100	200	400
Ratio	6:1	6:1	6:1	5.8:1	3:1
100 μ					
Line Flux	192	300	600	1200	2352
Background Flux	64	100	200	400	800
Ratio	3:1	3:1	3:1	3:1	2.9:1

(b) As a corollary, the same signal-to-background ratio is obtained if the entrance slit is wider than the exit slit, or vice versa.

To confirm this theoretical argument, data taken on a recording spectrometer are shown in Figures 2 and 3. In Figure 2 the signal strength from a *spectral line* is plotted as a function of entrance slit width, for a series

of fixed exit slits. The measurements were made on a 500 mm Ebert scanning spectrometer with long slits, which resulted in basic line breadths of about 25 microns due to diffraction and aberrations alone, as contrasted to 8 microns assumed in the theoretical treatment above for large spectrometers. The contour of the illumination at the exit

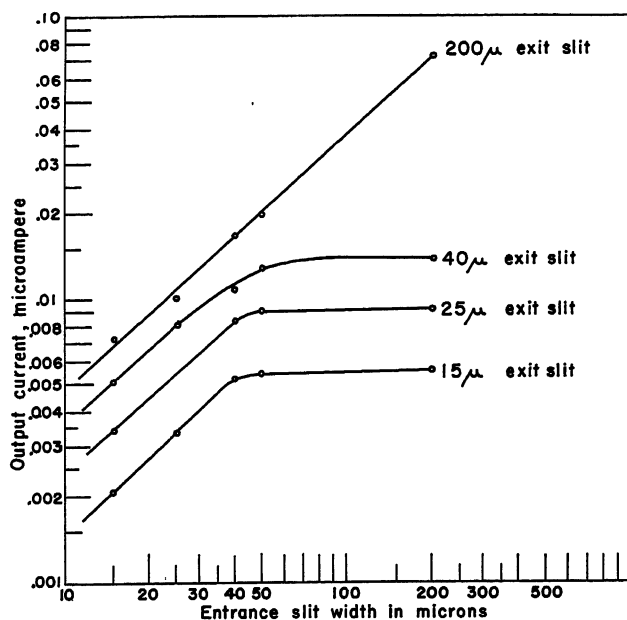


FIG. 2. Experimental effect of entrance slit width on line signal.

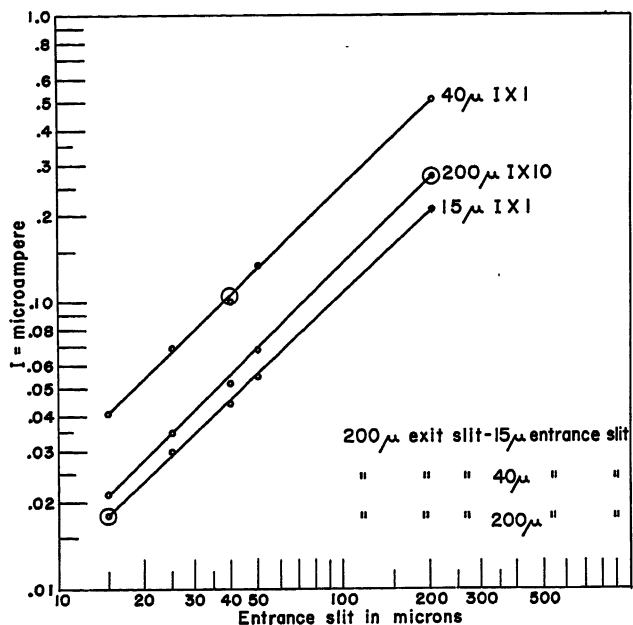


FIG. 3. Experimental effect of entrance slit width on background signal.

slit is not flat-topped at narrow entrance slit widths, but continues to rise to an effective value equal to the exit slit setting plus the aberration broadening, i.e., approximately $40\ \mu$ for the $15\ \mu$ slit.

The flat portion of the curves for the narrow exit slits demonstrates that the illumination does not increase when the entrance slit is opened beyond the critical width. The curve for the $200\ \mu$ exit slit indicates how the signal strength may be improved by opening the entrance slit, although this curve also would presumably level off at about $225\ \mu$ if the measurements had been extended.

In Figure 3, the signal for continuous radiation (i.e., background) is plotted as a function of entrance slit width, for several exit slits. In this case, since the illumination is increasing as the entrance slit is opened, the signal continues to rise linearly, as expected. If the data had been plotted for a given entrance slit, the signal would increase linearly with exit slit. This means that if both slits are increased simultaneously, the

signal increases as the square of the slit settings.

Photomultipliers always give better precision if operated at levels of illumination well above dark current, so wider slits will yield better precision in measurements. At the same time, it is desirable to have the best possible signal to background ratio, particularly at residual concentration, and this implies narrow slits. A compromise has to be made, based on the individual analytical program. The best way to improve the signal strength, rather than to open the slit width, is to increase the slit height, if this does not seriously affect definition.

The entrance and exit slits cannot be made the same width because: (a) the lines cannot be centered in the exit slits or aligned parallel to them to better than a few microns; and (b) any slight shift in alignment will cause large changes in signal.

In practice it is usual to allow at least 25 microns difference between entrance and exit slits.

At residual concentrations, where distin-

guishing the line above the background is more important than high precision, it may be desirable to use 25 and 50 micron slit combinations. For higher concentrations, 100 and 150 micron slits may be entirely feasible and will give greater quantitative reproducibility. Where both types of measurement are required simultaneously, a 50-micron entrance slit can be used with 25-micron exit slits for residuals, and 75 or 100 micron exit slits for higher concentrations.

Spectrometer Stability. The discussion of slit widths indicates the degree of stability required in the spectrometer. Since the entrance slit image is usually broadened by diffraction by 8 to 10 microns, a spectrum line from a 50-micron entrance slit can drift only ± 7.5 microns within a 75-micron exit slit, before the line edge begins to be cut off. Such stability requires a rugged construction, stress-relieved. The spectrometer must also be maintained at a constant temperature, to within a few degrees, for two reasons: (a) temperature changes will expand the frame, which can lead to a displacement of the spectrum, and (b) an increase in temperature will expand the glass blank of the grating or replica, producing a coarser spacing, reducing the angular dispersion. Not only will the entire spectrum be shifted, but the relative spacing of widely separated lines will be changed.

For these reasons, it is customary to regulate the room temperature to within a few degrees and to insulate or temperature-control the spectrometer itself. Otherwise, it is necessary to use wide slits, to allow more latitude for line shifts. Frequently, a means is provided for periodically or constantly checking the spectrum alignment, or even for maintaining the alignment automatically. Such realignment of the spectrum can compensate for shifts of the spectrum as a whole, but cannot correct for changes in dispersion, particularly if an extended wavelength range is covered by the exit slits.

Setting Exit Slits. Exit slits can be set approximately in position, to within $\frac{1}{4}$ or $\frac{1}{2}$ mm, by a wavelength or millimeter scale, or from a photograph. Each slit must then be oriented parallel to the line and centered on it, to within a few microns, by (a) moving the slit precisely with a screw drive; (b) tapping lightly on one side of the slit till a dial indicator on the other side shows the desired shift; or (c) rotating a "refractor" plate of quartz, which shifts the image of the line.

The adjustment must be made for the top and for the bottom of the exit slit. This final setting of the slit is made by burning a sample containing a high concentration of the desired element, and observing the photomultiplier response on a sensitive electronic voltmeter or oscilloscope. Such adjustments must be made with the photomultipliers in darkness.

Types of Mounting. Since astigmatism has no disadvantage for direct-reading measurements and since the wavelength range is fixed, the concave grating makes an ideal dispersing element for direct reading spectrometers. In the United States gratings have been used exclusively. Applied Research Laboratories, Baird-Atomic, and Jarrell-Ash use Eagle or Abney Rowland circle mountings. Jarrell-Ash has also used a "dual deck" Wadsworth mounting in which two concave mirrors are used to illuminate a single concave grating, to produce two identical spectra, one beside the other. This provides greater space for mounting exit slits and photomultipliers. Applied Research, Baird-Atomic, and Jarrell-Ash also supply photographic grating spectrographs which can be converted to direct reading instruments.

In Europe, Hilger and Watts, Manufacture Belge de Lampes et de Matériel Électronique (MBLE), and Optica use grating spectrometers for direct reading. Applied Research also manufactures in Europe. Radio Cinema uses a Jobin & Yvon prism spectrom-

eter for its Spectrolecteur, while Hilger & Watts has employed a medium quartz spectrograph for a direct reader for nonferrous metals. In Japan Shimadzu has employed a 1.5 meter spectrometer like the ARL.

Irradiation of Photomultipliers. If the sensitivity of the photosensitive surface of a multiplier phototube is measured by recording the photoelectric current, as a narrow intense beam of light is scanned across the photocathode, it will be found that the sensitivity increases greatly in the center and shows quite marked microvariations. For this reason, if the exit slit is imaged on the photosensitive surface, the phototube must be adjusted rather carefully for maximum sensitivity and must then be maintained in exact alignment. Alternatively, the light beam can be allowed to diverge to five or six millimeters before striking the photosensitive surface. The output current will then be relatively insensitive to minor shifts in the position of the light beam.

Integrating Direct-Reader Electronics

Two basic procedures have been developed for measuring the output of a multiplier phototube, integrated over a significant time interval: (1) The photomultiplier currents charge a series of capacitors, until the exposure is terminated, and then the voltage or charge on the capacitors is measured, one after the other, and (2) each photomultiplier current is converted into a series of pulses which actuate scalars or other counting devices. While the detailed circuitry, including the programming arrangements, becomes quite complex, the basic principles can be explained rather briefly.

Charged Capacitors. Among the methods used for reading out the voltage, or charge, on a capacitor are the following.

Electrometer Amplifier, Strip Chart Recorder. Applied Research Laboratories measures the voltage on each capacitor sequentially by a high-impedance electrometer amplifier

and strip chart recorder. During the exposure, the charge accumulating on the internal standard capacitor is recorded continuously. The exposure terminates when the recorder pen reaches 100. The charge on each capacitor is then indicated, in turn, at approximately two second intervals, by the pen deflection. Zero and sensitivity controls are provided for each element. Concentrations can be read directly off specially printed strip chart paper.

Amplifier and Meter. Hilger & Watts, for its Medium Polychromator, uses a high-impedance amplifier and sensitive microvoltmeter. A stepping switch automatically connects the meter successively to the individual capacitors, at approximately three-second intervals. Readings are converted to concentrations by graphs or tables.

Time of Discharge. Baird-Atomic adopted a circuit developed by Saunderson and Caldecourt⁵ at Dow Chemical Company. During the timed exposure, the photomultiplier outputs charge capacitors for both the analytical lines and the internal standard line. The intensity of the internal standard line and the capacity of its capacitor are chosen to produce a higher reference voltage than will accumulate on any of the analytical capacitors. At the completion of the exposure, the reference capacitor starts to discharge through a fixed resistor, R , and clocks for each of the analytical channels start to operate. As the voltage on the reference capacitor becomes equal to the voltage on an analytical capacitor, the corresponding clock is stopped. In other words, each clock measures the time required to discharge the reference capacitor to the voltage of the appropriate analytical capacitor. This time is proportional to the logarithm of the relative intensities, since the rate of discharge of a capacitor is given by $t = RC \ln (E_s/E_x) = RC \ln I_s/I_x$, where R is the fixed resistor, C the capacitance of the reference capacitor, and E_s and E_x represent the voltage of the reference and unknown capacitors.

A detailed description of the use of this instrument is given in J. Saunderson's article.⁵

Time to Match the Voltage. Hilger & Watts uses a system in which a quartz crystal oscillator drives a scaler until a regulated power supply charges a reference capacitor to the same voltage as the analytical capacitor, which stops the count. The scaler reads out up to four digits. The count is a linear function of the intensity. The programming circuit then moves on to the next capacitor.

Counts to Discharge the Capacitor. Jarrell-Ash employs a circuit which measures the charge on the capacitor by discharging it through a "multivibrator", which converts the energy into a series of pulses the frequency of which is proportional to the current strength. The pulses are counted by a four-digit scaler, until the voltage on the analytical capacitor drops to a given reference voltage, which stops the count. The scaler reading is directly proportional to the charge, that is, to the light intensity.

Photomultiplier Current Converted to Pulses. The electronic system used with the larger Jarrell-Ash direct readers converts the photomultiplier output directly into pulses by means of a "multivibrator". The latter consists essentially of a low-capacitance capacitor, typically .005 microfarad, which charges rapidly to a few volts, then discharges through a trigger tube, returning to ground, starting to charge once more, and continually repeating the process at up to 50,000 cycles/second. The transmitted pulse is shaped and amplified and drives either a four-digit scaler or a high speed pulse motor which turns a clock hand. The exposure is terminated when the internal standard channel reaches a given count. Then each scaler or clock dial is arrested at a count which is proportional to intensity. This is the fastest of all circuits, since all readings are available immediately after termination of the exposure.

Excitation for Direct Readers

Since in most cases precision and speed of analysis are primary aims in direct reading spectrochemical analysis, high voltage sparks, or condensed arcs, are most frequently used, followed by ignited arcs. The DC arc is employed only when other sources do not have the required sensitivity. The discharge is usually initiated and terminated by the programming circuit. In most cases the exposure is determined by the integrated flux to the internal standard exit slit. At times, particularly if an internal standard has to be added to each sample, a constant time of exposure is employed. Sometimes the analytical accuracy so achieved approaches 1%.

Almost always the specimens are mounted in exact position in the sample stands and are not re-adjusted during the exposure.

Direct-Reading Spectrochemistry

Precision. When the measuring circuits described are properly engineered, they should be capable of giving repeatability figures as follows:

	Coefficient of Variation
Electronic Signal	$\pm .1$ to $.2\%$
White light or mercury lamp	$\pm .2$ to $.3\%$
Non-segregated sample, measured for concentration levels above about .5%	$\pm .5$ to 1.5%
Sensitive elements in a non-segregated sample, measured for concentration levels in the range .1%-.01%.	± 2 to 5%
Non-segregated sample, for concentrations at limit of photographic detectability	± 25 to 100%

Sensitivity. The sensitivity of direct reader techniques seems about equal to that for photographic spectrographs. The sensitivity is affected by the choice of slit widths, as pointed out above. The author does not know of any claims that direct-reading sen-

sitivity exceeds that of photographic procedures, and the general consensus seems to be that there may be a loss in sensitivity by a factor of two to four times. The sensitivity limit has been defined as the concentration at which the coefficient of variation becomes $\pm 25\%$.

Choice of Lines. There are several essential differences between the procedures for choosing suitable spectrum lines for accurate quantitative spectrochemical analysis by direct reading methods and by photographic spectrographs. It is impractical to use as many lines, since each new line involves at least another costly exit slit, multiplier phototube, and power supply connection, and since there is a physical limit to the number of exit slits which can be mounted in a given length of focal curve. On the other hand, any given spectral line can be measured over a much greater intensity range, both because the output of a multiplier phototube is linear over approximately a 10,000-fold range of intensities (compared to a 100-fold latitude for a photographic emulsion), and because the light flux transmitted by a slit will still continue to rise, even in the presence of self-reversal (whereas self-reversal photographically usually produces a drop in the microphotometer deflection). A direct reader will yield its highest precision with lines that are so strong they would produce densities in the range of 2.0 to 4.0 in a normal photograph of comparable exposure time; whereas best results are achieved photographically for lines in the density range 0.3 to 0.7.

(a) *Analytical Lines.* A strong line (usually the most sensitive line) of an element will normally be used to measure concentrations in the range of residual up to 3 or 5%, unless there is an interference from the matrix or other elements possibly present. A less sensitive line may be used for the range 3%–20%, and a third above 20%, but in all cases the lines should give a strong signal, as contrasted to photographic practice, where

relatively weak lines must be used to permit precise measurement.

(b) *Internal Standard Line.* In contrast to photographic practice, where several internal standard lines are used, closely matched in intensity, wavelength, and excitation potential to the individual analytical lines, in direct-reading techniques a single strong internal standard line is employed to control the exposure for all analytical lines. Sometimes the "raie ultime" of the internal standard element is employed, but it is better practice to utilize a line of intermediate sensitivity, which will be free of self-reversal and self-absorption. Since the photomultiplier response is linear and the gain for each analytical line can be individually adjusted, wavelengths do not need to be matched. The requirement for closely matched excitation potentials between internal standard and analytical lines does not seem to be as exacting as in photographic work. Possibly too little attention is paid to selecting matched lines. Certainly excitation potentials should be matched within the limitations imposed by practical considerations of slit placement, line interferences, and sensitivity.

Speed and Cost of Analysis. By direct-reading procedures an individual operator can analyze a single sample for, say, ten elements in about three minutes after receipt of sample in the case of pulse-driven clocks, or in six minutes with the scanning in time technique. This contrasts with six-eight minutes for a team of three or four operators, or twelve to fifteen minutes for an individual, using high-speed photographic methods. A series of samples can be run by single operators in an average elapsed time of two and one-half to six minutes by direct readers, compared to nine–twelve minutes photographically. Despite the higher capital expenditure, direct reading spectrometers will normally pay for themselves either by (a) permitting close furnace control of a melt, or (b) by reduced operating costs, if

the number of routine analyses exceed 25 to 50 in a day.

Vacuum Direct Readers

Mitteldorf's article on Vacuum Spectroscopy discusses the significance of the vacuum ultraviolet region for photographic work. In direct-reading spectrometry, Applied Research Laboratories, Hilger & Watts, MBL, Optica, Shimadzu, and Jarrell-Ash have developed instruments for this region, specifically for the analysis of C, P, and S in ferrous alloys. These instruments are different from standard integrating direct readers in the following respects:

The Spectrometer. For structural stability and vacuum tightness, the spectrometers are built into cylindrical steel tanks. The Hilger & Watts instruments employ three fluorite prisms; all the others use concave gratings of 1.5 or 2-meter radius of curvature. Linear dispersions run from about 7 Å/mm in the case of the ARL to 4 Å/mm in the Jarrell-Ash. The spectral range usually starts at about 1600 Å, to include C 1625 Å. One Hilger & Watts instrument, specifically for C, P, and S, covers only the vacuum ultraviolet. The ARL and most others cover up to 3300 Å. The Jarrell-Ash extends to 4025 Å. The spectrometers are usually evacuated by only a mechanical pump, to a pressure of 1 to 5 microns. However, in this pressure range the transmission of the far ultraviolet lines will be considerably less than 50%, and will be quite variable, whereas pressures in the range 10^{-3} or 10^{-4} mm Hg will increase and stabilize the transmission at essentially 100%.

Excitation. A high-voltage spark has insufficient sensitivity and too high a background for the low concentrations of C, P, and S required in steel analysis. Accordingly, a "Multisource" or ignited arc is used.

The Sample Stand. The oxygen of the atmosphere must be reduced to a low level in the spark stand. The stand consists of a chamber of vacuum-type construction,

which is flushed with flowing argon gas, to sweep out the oxygen. The discharge takes place in argon. It is common to use a counter-electrode of silver, redressed after about 20 samples. If the sample is not kept scrupulously clean, the discharge is likely to be weak and will give erratic results. A fluorite lens or window is used, and must be kept clean.

The Detector. The multiplier phototube must have a thin, high-purity quartz window to transmit down to 1600 Å, with high sensitivity and low dark-current. EMI 13-stage tubes have been employed generally, at least for the vacuum ultraviolet lines.

Spectrochemical Results. Typical spectrochemical results are:

Element	Concentration range %	Mean Deviation %
C	.010	.001
	1.50	.02
P	.005	.001
	.050	.004
S	.005	.001
	.050	.003

Sequential Integration

The fifth technique for direct-reading spectrochemical analysis, a procedure which combines integration measurements with a sequential scan through the spectrum, has been described by Hasler.⁶ A phototube samples part of the undispersed radiation through the entrance slit, and acts as the reference channel, to obtain integration over approximately $10''$. The exit slit and multiplier phototube are set sequentially on each element line, and the analytical capacitor accumulates a charge. At each new line another exposure of about $10''$ is run, controlled in fact by the reference channel. The integrated intensity for the analytical line is then determined by measuring the voltage on the capacitor by means of a high impedance amplifier and strip chart recorder.

The procedure is relatively slow and labo-

rious, and the results not quite as accurate as simultaneous integrated measurements.

REFERENCES

1. FASTIE, W. G., *J. Opt. Soc. Am.*, **42**, 9, 641 (1952).
2. BROIDA, H. P. AND MORGAN, G. H., *Anal. Chem.*, **24**, 799 (1952).
3. BROIDA, H. P. AND CHAPMAN, M. W., *Anal. Chem.*, **30**, 2049 (1958).
4. FERGUSON, R. E. AND BROIDA, H. P., *Anal. Chem.*, **28**, 1436 (1956).
5. SAUNDERSON, J. L., CALDECOURT, V. J. AND PETERSON, E. W., *J. Opt. Soc. Am.*, **35**, 681 (1945).
6. HASLER, M. F., *Spect. Acta*, **6**, 76 (1957).

R. F. JARRELL

DOUBLET SPECTRA*

The extension of the concepts developed for hydrogenic spectra to arrive at an explanation of complex spectra is natural and logical. An appropriate intermediate step is to consider the relatively simple doublet spectra that have been mentioned in connection with the empirical discussion of Rydberg and similar series formulas. Such spectra originate in atoms or ions having a structure or charge configuration characterized by a single active external electron. These configurations differ from that of hydrogen by having an inner core of electrons surrounding the nucleus. As in the instance of hydrogen the energy states assumed by the active or, as it is sometimes called, the valence electron, are identifiable with the spectral terms.

Before discussing the assignment of quantum numbers to the valence electron and the resultant specification of energy states to this limited class of spectra, it is desirable to describe briefly the electron configurations of the elements following the systematic development of the scheme as one goes through the periodic table in the order of increasing atomic number, this number, of course,

* The fourth in a consecutively developed series of articles on fundamentals of optical Emission Spectra: see *Introduction: Designation and Description of Spectra* for list of topics, p. 202.

being equal, for each neutral atom, to the total number of electrons outside the nucleus. The electrons entering into the general configuration are sufficiently described by two quantum numbers n and l . The total quantum number n serves to locate the electron with reference to the nucleus. These total quantum numbers, which are integers beginning with 1, are associated in the conventional language with a series of shells, named according to a notation borrowed from X-ray spectra, K, L, M, N, O, and P. All electrons in the same shell have the same value of n . The azimuthal quantum number l , associated with the orbital angular momentum, takes integral values beginning with zero. In the current notation an electron of a particular l -value is indicated by a lower case italic letter. These classes of electrons are shown as follows:

l	0	1	2	3	4	5...
designation	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i> ...

The assignment of l values is also systematized. The system now regarded as correct is that proposed by Stoner.¹ It was later found to be fully in accord with the Pauli exclusion principle, an empirical generalization to which there will be further reference. According to the scheme there is a definite number of electrons in each complete shell, and this number is made up of a fixed distribution, among the various l -values. For instance, for the first or K-shell there are two *s*-electrons, for the second or L-shell there are two *s*- and six *p*-electrons, and for the third or M-shell there are two *s*-, six *p*-, and ten *d*-electrons, and so on. The number of electrons of the same n - and l -value, called equivalent electrons, is indicated in the notation by a small number written as an exponent. Complete tabulations of the electron configurations for all atoms concerning which there is available information are contained in the general references listed. The more recent tabulations are to be preferred in the instance of elements of atomic number 90 and

higher since the elements thorium, protactinium and uranium begin a second series of rare earths characterized by the progressive filling of the 5*f*-shell, an experimental fact established since the earlier tabulations appeared. The most up-to-date tabulations are to be found in the "American Institute of Physics Handbook,"² and in the "Key to the Periodic Chart of the Atoms," prepared by Meggers.³ The various groups are not always filled in order. For instance, the 4*s* and 4*s*² configurations corresponding to potassium and calcium are completed before the filling of the 3*d*-shell to complete the first long period. Similarly rubidium and strontium characterized by 5*s* and 5*s*² appear ahead of second long-period elements having a configuration containing 4*d*-electrons in increasing number. The filling in of the 4*f*-electrons to establish the first family of rare earths interrupts the binding of the 5*d*-electrons to complete the third long period.

Let us now turn our attention to the alkalis for which normal electron configurations may be tabulated as follows:

assumes all possible values of *n* for each *l* value. A spectral term or energy value is associated with each of these configurations. In notation now universally adopted, a capital letter is used to designate a term. Thus *S* is the term associated with an *s*-electron. Since all such terms are doublets a superscript 2 is written before the term designation. This shorthand convention may be summarized:

Electron	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>
Term	² <i>S</i>	² <i>P</i>	² <i>D</i>	² <i>F</i>	² <i>G</i>

The interpretation and representation of the components of the doublet structure, or levels as they are now called, remain to be considered. The term values, as has been pointed out, may be expressed in wave number units by the Rydberg formula $R/(n + \mu)^2$ for spectra of neutral atoms. The factor 4 is required for singly ionized atoms, 9, 16, and so on for the second, third, and higher states. The energy may be converted to volts according to the approximate relation $V(\text{volts}) = 12345 \times 10^{-8} \nu$. The term

<i>n</i>	1	2	3	4	5	6	7
Li	1 <i>s</i> ²	2 <i>s</i>					
Na	1 <i>s</i> ²	2 <i>s</i> ² 2 <i>p</i> ⁶	3 <i>s</i>				
K	1 <i>s</i> ²	2 <i>s</i> ² 2 <i>p</i> ⁶	3 <i>s</i> ² 3 <i>p</i> ⁶	4 <i>s</i>			
Rb	1 <i>s</i> ²	2 <i>s</i> ² 2 <i>p</i> ⁶	3 <i>s</i> ² 3 <i>p</i> ⁶ 3 <i>d</i> ¹⁰	4 <i>s</i> ² 4 <i>p</i> ⁶	5 <i>s</i>		
Cs	1 <i>s</i> ²	2 <i>s</i> ² 2 <i>p</i> ⁶	3 <i>s</i> ² 3 <i>p</i> ⁶ 3 <i>d</i> ¹⁰	4 <i>s</i> ² 4 <i>p</i> ⁶ 4 <i>d</i> ¹⁰	5 <i>s</i> ² 5 <i>p</i> ⁶	6 <i>s</i>	
Fr	1 <i>s</i> ²	2 <i>s</i> ² 2 <i>p</i> ⁶	3 <i>s</i> ² 3 <i>p</i> ⁶ 3 <i>d</i> ¹⁰	4 <i>s</i> ² 4 <i>p</i> ⁶ 4 <i>d</i> ¹⁰ 4 <i>f</i> ¹⁴	5 <i>s</i> ² 5 <i>p</i> ⁶	6 <i>s</i> ² 6 <i>p</i> ⁶	7 <i>s</i>

The probable configuration of the artificially produced radioactive alkali, francium, is obtained by adding 7*s* to the radon configuration. Owing to its short life and inavailability of a sufficiently large sample, its spectrum has not been observed. It is the single outer electron that is responsible for the characteristic features of these spectra. In the normal or unexcited configuration the valence electron is in an *s*-state. Between this state and complete removal or ionization a large (theoretically infinite) number of states is possible in which the electron

formula is comparable to the special form R/n^2 for hydrogen. The interpretation of the integer *n* in the hydrogen formula as the total quantum number is not directly transferable to the Rydberg formula in its historic form which was adopted many years before the development of quantum theory. When written in the form $R/(n + \mu)^2$ the value of *n* is always smaller than the total quantum number in R/n^2 for the equivalent position of the valence electron in the hydrogenic case. To make the respective values of *n* represent total quantum numbers, it is

EMISSION SPECTROSCOPY—LIGHT

necessary to write the Rydberg term formula, $R/(n - \mu)^2$, in which the expression in parentheses is called the effective quantum number, represented in equivalent form by $\sqrt{R/\nu}$. When following this usage, μ is

called the quantum defect. It compensates for the screening effect of the core of electrons surrounding the nucleus. It would have been more logical to make the correction to the nuclear charge in the numerator,

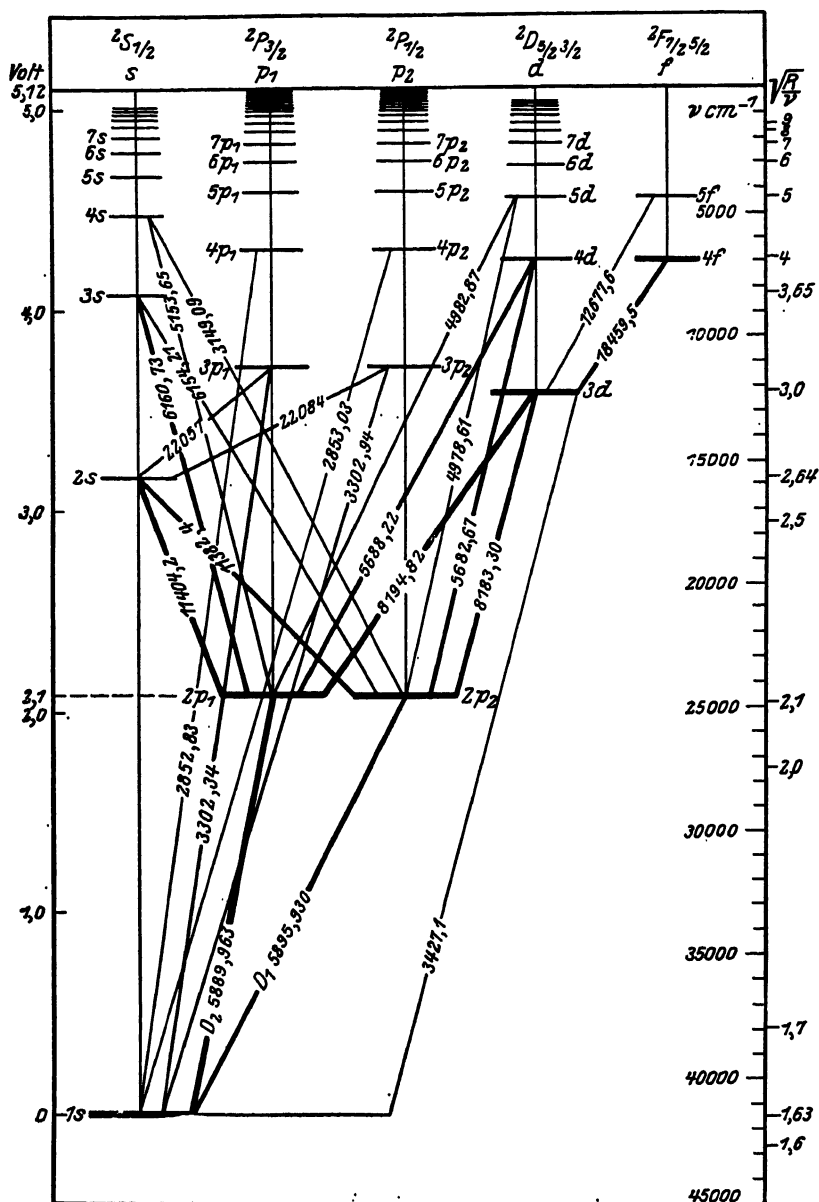


FIG. 1. Energy levels of the sodium atom according to Grotrian. Effective quantum numbers are shown at the right margin. Wavelengths in angstroms appropriate to illustrated transitions are noted. Doublet differences are too small to be represented on this scale.

which is actually done in formulations for separations of term levels, but in the instance of the term formula, the historic pattern is followed. In general, the quantum defects are larger for terms of low l value and tend to vanish as l increases. Terms with l -value 3 or f -terms and, of course, all those with larger l are very nearly hydrogenic. This is obviously in harmony with the Bohr model when we note that the smaller the value of l , the greater the elongation of the orbit and penetration of the core. For sufficiently large l the orbit becomes circular and the configuration approximates the hydrogen case with the core electrons balancing all but one unit of the positive nuclear charge.

The term "structure" is most effectively visualized by use of a term diagram or in the sense of its physical meaning an energy-level diagram. In such a diagram the positions of the levels are plotted by measuring downward from the ionization limit. When the permitted transitions are drawn in as slant lines, the plot is called a Grotrian diagram, named for the author of an extensive set of such diagrams for well-known spectra.⁴ Figure 1 is a Grotrian¹⁹ diagram for Na I with the energy level plot for hydrogen alongside. The doublet separations cannot be represented accurately on this scale.

The absolute value of the lowest term,

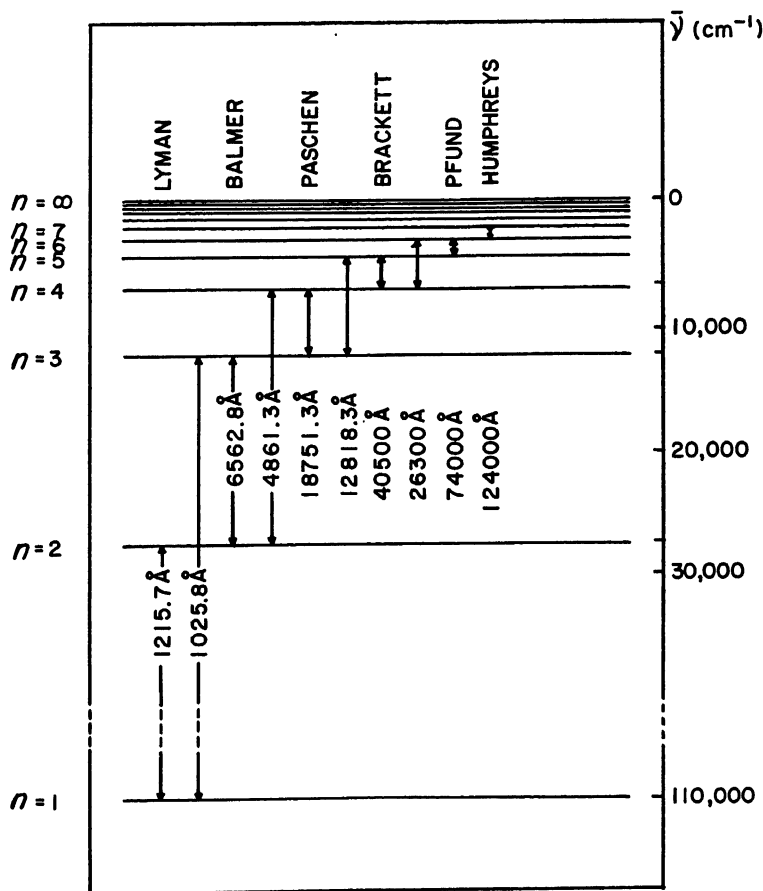


FIG. 2. Energy levels of the hydrogen atom. Wavelengths in angstroms of the lines associated with the transition corresponding to the first lines of the various series are listed.

always the lowest ^2S term in alkali spectra, is equivalent to the ionization potential. It may be calculated for Rydberg-type series if any two members of the principal series in the form $\nu_i = n_i^2S - m_i^2P$ can be observed. If a Ritz equation is followed, three series members are needed.

Transitions either for absorption or emission follow fairly simple rules. There is no limitation on changes in n . When an electron jumps from one orbit to another, the azimuthal quantum number changes by 1, that is $\Delta l = \pm 1$. Thus the term transitions are $^2S \leftrightarrow ^2P$, $^2P \leftrightarrow ^2D$, $^2D \leftrightarrow ^2F$, and so on. Since the terms are all doublets, the problem of intersystem transitions between terms of different multiplicity does not arise. There is also a rule governing the transitions involving different levels of a term which is taken up in connection with the following discussion.

Early in the development of atom mechanics, it became necessary to introduce another angular momentum in the atom in addition to the angular momentum in the valence electron. At first ascribed to the atom core, this angular momentum was attributed to an electron spin by Uhlenbeck and Goudsmit. This interpretation is now universally accepted. The spin angular momentum is also quantized in units of $\hbar/2\pi$ and the spin quantum number is designated s , always equal to $1/2$ for a single electron. The two angular momenta, l and s combine vectorially to give a resultant quantized angular momentum j . Since s is always $\pm 1/2$, j is always $l \pm 1/2$, so that the two values of j correspond to the two levels of the doublet. The S term is physically single since $l = 0$ and j has only one value, namely $1/2$. We thus get the following quantum numbers for doublets:

	l	j
^2S	0	$1/2$
^2P	1	$1/2, 3/2$
^2D	2	$3/2, 5/2$
^2F	3	$5/2, 7/2$

The selection rule for j is $\Delta j = \pm 1$ or 0. The j -value appropriate to a level is written as a subscript following the term designation. For instance, the doublet P levels are written $^2P_{1/2}$ and $^2P_{3/2}$.

A doublet is a special case of a multiple term, called a multiplet. This is the preferred use of the terminology although "multiplet" is frequently used to designate an array of lines resulting from a transition between multiple terms. Multiplet separations are due to the energy of interaction between spin and orbital magnetism of the electrons. The value of this energy for a single electron is indicated by γ and is given by the formula

$$\gamma = a l^* s^* \cos(l^* s^*)$$

The factor a is called a separation factor. It is constant for a given term and in the instance of a hydrogenic configuration is given by

$$a = R\alpha^2 Z^4 / n^3 l(l + 1/2)(l + 1)$$

where α is the fine-structure constant. The cosine term is the cosine of the angle between the quantum vectors having a resultant j . The familiar trigonometric form is

$$\cos(l^* s^*) = \frac{j^2 - l^2 - s^2}{2}$$

Introducing the quantum-mechanical expressions for the starred quantum designations, in accordance with previous discussion of the azimuthal quantum number, l , a modified form, discovered empirically by Landé, is obtained, namely

$$\cos(l^* s^*) = \frac{j(j+1) - l(l+1) - s(s+1)}{2}$$

The doublet separation is the difference between the two values of γ , corresponding to $j = l + 1/2$, and $j = l - 1/2$. This reduces to

$$\Delta\nu = \frac{R\alpha^2 Z^4}{n^3 l(l + 1/2)(l + 1)} (l + 1/2) \text{ cm}^{-1}$$

or

$$R\alpha^2 Z^4 / n^3 l(l + 1) \text{ cm}^{-1}$$

For non-penetrating orbits where the screening of the nucleus is large, but not quite complete, Z must be corrected by a screening constant and the formula is written

$$\Delta\nu = R\alpha^2(Z - \sigma)^4/n^2l(l+1) \text{ cm}^{-1}.$$

It is generally not possible to calculate σ and hence a directly, but σ follows a regular curve in a sequence of isoelectronic spectra. The method has therefore proved extremely useful in predicting and identifying separations in highly ionized spectra. Numerous publications on isoelectronic sequences by Millikan and Bowen and by Gibbs and White in the mid-twenties illustrate the method. For penetrating orbits, separate screening constants appropriate to the inner and outer portions are required and the formula is modified to read

$$\Delta\nu = R\alpha^2(Z - S_0)^2(Z - S_i)^2/n_i^2l(l+1) \text{ cm}^{-1}$$

Formulas have been derived theoretically for the relative intensities in multiple groups. In the instance of a principal series doublet the intensity ratio corresponding to higher and lower j -values is 2 to 1. In general, this rule is followed closely for the first members of the series. In applying the general rule an array is set up in which each level is associated with a number equal to the quantum weight of the state given by $2j + 1$. This is illustrated by an array for the $^2P - ^2D$ transition

	$^2P_{3/2}$	$^2P_{1/2}$
	4	2
$^2D_{5/2} \ 6$	X	0
$^2D_{3/2} \ 4$	Y	Z

The unknown intensities are represented by X, Y, and Z. The zero is in the position of the forbidden transition. The following relationships apply:

$$\frac{X}{Y+Z} = \frac{6}{4} \quad \text{and} \quad \frac{X+Y}{Z} = \frac{4}{2}$$

This is satisfied by $X = 9$, $Y = 1$, and $Z = 5$. Experimental results are in reasonably good agreement.

REFERENCES

1. E. C. STONE, *Phil. Mag.*, **48**, 719 (1924).
2. "Am. Inst. Physics Handbook," McGraw-Hill, N. Y., 1957.
3. W. F. MEGGERS, "Key to the Periodic Chart of the Atoms," W. M. Welch Mfg. Co., Chicago (1958).
4. W. GROTRIAN, "Graphische Darstellung der Spektrum von Atomen und Ionen mit ein, zwei, und drei Valenzelektronen," Springer, Berlin (1928).

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ELECTRODES—EFFECT ON ACCURACY. See ACCURACY IN SPECTROCHEMICAL ANALYSIS, p. 99.

ELECTRONICS INDUSTRY APPLICATIONS

In the electronics industry, the connection between spectroscopy and standardization is straightforward. Instead of controlling the composition of a single alloy, however, the spectrographer is called upon to examine almost every material that finds its way into a vacuum tube or other electronic component. Trace elements in Ni cathodes ultimately determine the emission of electrons, thus the behavior of a particular tube. Upon the impurities in Ge or Si depends the very functioning of the transistor of which it is the heart.

In general, the emission spectrograph can detect elements in the ppm range, while elements are known to have electronic effects in the ppb range. Si, for example, is sold on the basis of its B content. DuPont has three grades of the transistor grade material in which the B content is guaranteed to be less than 7.1, 3.5 and 1.8 ppb, respectively. Directly the spectrograph can detect about 100 ppb and so concentration techniques must be employed, one of the best perhaps being that devised by Morrison and Rupp at Sylvania.¹ With regard to Si as well as other solid-state materials, the ultimate criterion is their electrical properties, and materials are sold with performance rather than chemical specifications. But techniques for the latter

are required in order to predict and assure proper performance.

At Sylvania Research Laboratories, Morrison and Rupp have made considerable progress. Taking silicon carbide as the base—it is one of the promising high-temperature semiconductors—they have reported greatly improved sensitivities ranging from 1–5 ppb for Ag and Be to 100–500 ppb for As, Ge, Hg, P, Sb, Sn and Zn.² Their technique has not been to seek a panacea whereby, with a single gadget or technique, the sensitivity of all of the elements would be miraculously improved. Instead, they have taken step-by-step measures each having small effect but used together the results are cascaded. Carbon electrodes are used rather than graphite; exposure times are matched to the burn-off of the individual elements; an argon atmosphere is used to enhance the sensitivity of certain elements. Present studies are being made with a high-speed spectrograph; exposure of the order of one-tenth second is possible for such volatile elements as As and Hg in order to optimize their signal-to-noise ratios.

Such techniques are currently limited to research. Trace-element determinations in transistors are now commonplace on the production line. The Ge wafer is a slice of a single crystal oriented along the 1, 1, 1 axis. Once sliced, the wafer, about $\frac{1}{16}$ " on a side and 0.010" thick, is etched to size either chemically or electrochemically. The starting material for the Ge is germanium dioxide almost spectrographically pure which is reduced in a hydrogen furnace, zone refined, doped with a trace of Sb, In, or As and finally grown into a single crystal. To obtain the desired semiconductor properties, "impurity dots" of In or Pb about 0.008" in diameter are fused to each side of the Ge wafer. Leads are soldered to the dots and also to the solder-dipped Ni base which not only supports the assembly but also acts as a heat sink.

To minimize the high rejection or "shrink-

age" rate of transistors is the goal of the quality control department. Accordingly, the emission spectrograph, among an assortment of electronic testers and other analytical tools, has become an integral part of the assembly line; its job is to predict and locate brewing trouble. In many plants the quality control program calls for the spectrographic analysis of almost every raw material. Everything including the incoming germanium dioxide, lead wires, impurity dots and solders is scrutinized before being released to the production department.

It is interesting to note that alone, a resistance check on a test bar of Ge is not a foolproof test because elements in Group III and V tend to offset one another and certain nonionizable ones like Si do not affect the resistance. A spectrographic test will often suggest such a situation. But long before the final transistor-grade bar is made, the spectrograph is put on the job. The starting material, germanium dioxide, must show a Si content of less than 10 ppm and all other elements must be undetected. Of course, to the spectrographic tests are added others such as bulk density measurements, the presence of volatiles at 800°C and a microscopic examination.

Impurity dots are also carefully checked especially in view of the ever-present possibility of confusing the emitters with the collectors. The former consist of an In alloy generally containing Ga and doped with Ag or Zn while the collector dots are composed of pure In. Solder materials are important in that the wrong material may result in an unacceptably high resistance to ground.

Much research today on transistors is centered around high-temperature applications. Needed especially in military applications are transistors capable of operating at temperatures up to 1000°C. Theoretically, the "three-fives"—compounds of Group III and V elements—should be superior in this respect. One such three-five, gallium arsenide does, indeed, appear promising but good

transistors have not, as yet, been made consistently from it. In diodes, however, where purity requirements are not so stringent, gallium arsenide has already found a niche.

One trace-element job of the spectrograph is detecting the undetectable in, say, spectrographically pure Ga. Before purification, the Ga is analyzed and after the first zone refining pass, both ends and the center section are again analyzed. Impurities may either migrate to one end or the other or not move at all during the initial pass. These impurities are detectable spectrographically in the first zone refining pass and an analysis often furnishes clues to the engineer who wants to know how many passes will ultimately be required and whether certain elements migrate altogether. Before the impurities dip below sensitivity levels, spectrographic determinations provide data which are then extrapolated.

In a concerted effort to produce purer gallium arsenide, every operation is being carefully scrutinized. Transistor grade etching acids are further distilled in quartz stills, the purification followed by the rotating disc technique of analysis. One refinement for detecting lower concentrations of impurities is the hollow cathode in which elements are excited over and over again instead of being lost up the stack. Initial experiments with traces of Fe have been encouraging.

There is interest in another Group III element which, presumably, could be coupled with one in Group V. This is B and a recent report by Harvey³ indicates a general cracking of its sensitivity barriers. For example, he reports detection limits of about 0.5 ppm for Mg, Cu, Cr and Ca using a 1.5-m spectrograph which figures, when translated to larger, more modern spectrographs, would probably mean 0.05 ppm. Harvey, like Morrison and Rupp, has chosen to optimize many conditions to obtain higher sensitivity rather than concentrating on but one. Each element and matrix is treated as a separate problem. For some he finds the Stallwood

jet useful; for others atmospheres other than air.

Not all of the work in semiconductor materials is on traces. As mentioned, impurity dots are usually In alloys, the composition of which has to be closely controlled. Hyman⁴ reported on the determination of Ga, Zn, Ag and Al in In alloys and has stated that several other elements have recently been added to the porous cup method employed. For the determination of Ga in individual dots, Murt of Lansdale Tube Co., Lansdale, Pa., has developed a graphite spark technique soon to be published in *Applied Spectroscopy*. Here a single dot is dissolved and dried on the end of a flat-top graphite electrode where, after drying, it is sparked. Incidentally, trace elements as well as alloying constituents affect the properties of In and methods have been worked out for such determinations. Harry Hyman, at RCA Semiconductor Division, Somerville, N. J., will report in a future issue of *Applied Spectroscopy* on an a.c. arc method in which In is first dissolved and then allowed to dry on a shallow, center-post electrode. This technique permits the preparation of standards from solutions of high-purity In. Few metallic standards are currently available.

Because of the ease in standardization, solutions techniques are becoming increasingly popular despite the necessity for preliminary sample preparation. Old standbys such as the rotating electrode are still used and have a decided advantage when suspended matter is present or suspected (Sn in acid solutions, for example). When complete solution is effected, a number of spectrographers use the vacuum cup electrode (UCP 6010) originally suggested by T. H. Zink then at Armour Research Foundation in Chicago. With this electrode, the solution is sucked from a Teflon reservoir through a fine hole into the arc column. A similar method, originally proposed by W. M. Henry of Battelle Memorial Institute in Columbus, Ohio, uses a porosified electrode rather than

one with a hole drilled into it. The reservoir can be made from almost any plastic material but perhaps the easiest and cheapest source is the $\frac{1}{2}$ " dia. polyethelene caps used for plastic mixing vials. A hole is simply punched into the center of the cap through which the arc porosified electrode is pushed. The method has been found to yield working curves almost identical with those from the porous cup technique.

Vacuum Tubes

In the production of vacuum tubes, there is always the possibility that the wrong material will be used or that the material used is not up to standard. Month of the RCA Microwave Div., Harrison, N. J., recently presented a good example of this. On a magnetron tube was found a glassy deposit containing Mg, Al and Si. It turned out to be identical with the brick inside a furnace in which the tube was baked and a new kind of brick was quickly substituted. Magnetrons, incidentally, are made using OFHC (oxygen-free, high-conductivity) copper and all batches of this material are checked for impurities. A trace of a volatile element would be ruinous to tube operation.

In conventional electronic tubes, volatile elements must be carefully avoided, too. Coating the inside of the envelope, an element often makes it conductive and plays havoc with the electronic characteristics of the tube. When spotted, a bulb deposit is removed (dabbing with acid-wetted filter paper is one technique) and arced. In one such test recently at RCA, Ag was found and with a little further detective work, it was discovered that a Ni grid wire was wrongly flashed with Ag before being plated with Pd. Ni plating baths are another potential source of volatiles. So frequently are additives used in these baths as brighteners and anti-pitting agents that all new baths are suspected.

By far the most important part of a vacuum tube is the cathode—the source of

electrons. The usual method employed to obtain controlled emissivity is to spray the Ni shell with mixed Ba, Ca and Sr carbonates which are then converted to the oxides by heating as the tube is evacuated. The emissivity as well as the life of the tube depends not only on the composition of the mixed carbonates but also on that of the Ni base. Depending on its purity, Ni varies from active (99.5 % pure) to passive (99.99 % pure). Elements in the former, such as Si, Mg, Ti and Al, serve as activators for the carbonates. They not only increase the emissivity of the latter but also reduce the time required for activation. The use of passive Ni, on the other hand, results in lower emissivity but, of more interest in military applications, a longer life-time.

Through the work of Committee F-1 of ASTM, great strides have been made in standardization of cathode nickels in the industry. Three standards have been made available (the National Bureau of Standards supplies them) and analytical methods have been thoroughly cross-checked. The early method devised by Jaycox⁵ in which Ni is converted to a powder and mixed with graphite is still in widespread use although direct and solution techniques have also been proposed.

A new development in cathode technology is the introduction of Ni alloys (Co and Mo are two such constituents) to replace relatively pure Ni. The alloys are sprayed with carbonates and are used where high strength at high temperatures is needed in magnetrons, for example. Magnetrons are made with still another type of cathode called a matrix cathode which consists of a hollow sintered cylinder of W and Ba. The cylinder is slipped over the heater wire which, in turn, is packed with aluminum oxide.

Such techniques are used to secure maximum performance from tubes, because miniaturization, operation at higher temperatures and greater ruggedness are the by-words everywhere. RCA's Nuvistor is a recent

development along these lines. It is made completely of metal and ceramic, is a fraction the size of an ordinary receiving tube and has extremely high resistance to mechanical shock and vibration.

While Ni alloys are being used for greater strength cathode structures, a basic study is now under way on high-purity Ni at Sylvania Research Laboratories. The subject of activators is still more of an art than a science but, with the help of an Air Force contract, Sylvania is attempting to determine the effects of individual impurity elements on the Ni. Here the emission spectrograph is invaluable to metallurgists in adding tiny traces of elements to Ni metal.

As indicated earlier, volatilization inside an operating tube is often a fatal weakness and much research has been undertaken to prevent and inhibit the phenomenon. One notable study was made at RCA's Microwave Division by Joseph Antalec, using the new RCA X-ray spectrograph. Films of various alloys are evaporated and then compared with the base alloy. From these studies it is hoped to predict volatilization rates of the alloys and correlate them with the basic gas laws. As a non-destructive tool, the X-ray spectrograph is also being used for analyzing iron-nickel films which are finding application as tiny magnetic memory devices.

As all household appliance repairmen know, an eerily glowing vacuum tube usually indicates incipient failure. John A. Grosso of Tung-Sol, Bloomfield, N. J., described several instances where glows were analyzed spectrographically. In one receiving tube, by exciting the gas with a Tesla coil, he recorded the dim light using an exposure of several hours on a 103-F plate. Hydrogen lines were detected, indicating the presence of water vapor. In high-power tubes used at microwave frequencies any absorbed water vapor on the surfaces of glass or ceramic insulators may dissociate and release hydrogen to upset the operation of the tube. Leaks are another

source of trouble inside a tube. In a rejected neon indicator lamp Grosso detected nitrogen bands—strong circumstantial evidence of air leaking into the envelope. In a cold cathode tube carbon monoxide bands were detected—indicating the presence of organic materials, possibly oil from the vacuum pump. In a lamp filled with Kr and N, cyanogen bands were found, once more indicating oil vapor.

Kr may seem exotic to most spectrographers who would probably make some very careful measurements before reporting it. But in the tube industry almost any combination of elements is likely to be involved. In vacuum tube grid wires one is likely to encounter Fe, Mn, Mo in a Ni base (Hastelloys) or perhaps W-Mo alloy; Cu alloys containing Cr are used in grid supports; Zr, W or both are often alloyed with Ni in cathode alloys for high emissivity; Ba is the metal used in getters which, when flashed, traps residual gases. A really unusual combination of elements was recently used to seal lead wires in the ceramic base of RCA's Nuvistor. The base is dipped into a solution of Mo and Li salts and fired in hydrogen to reduce the Mo which adheres nicely inside the holes. The surfaces, also coated, are given a light grinding to remove the Mo.

Phosphors

With the advent of fluorescent lighting, then television and soon electroluminescent lighting, the production of phosphors has mushroomed over the past two decades. Most commercial phosphors are made from zinc sulfide or mixtures of co-precipitated zinc-cadmium sulfide in which small amounts of Cu, Ag or Mn behave as activators. The efficiency, lifetime, brightness and color are all severely affected by composition and close analytical control is called for with the spectrograph again taking a dominant position. Electroluminescence is fascinating as well as alluring because it offers hopes for panels of

flare-free light. Before these panels can be installed in the home, however, efficiency must be improved to compete with more conventional types of lighting. There is no question that research on different materials, activators and technique will someday make such lighting common but, thus far, the only large-scale applications are in automobile dashboard lighting and household night lights.

REFERENCES

1. MORRISON, G. H., AND RUFF, R. L., *Anal. Chem.*, **29**, 892, 1957.
2. MORRISON, G. H., AND RUFF, R. L., *Analysis of Impurities in Silicon Carbide*, a chapter in "Silicon Carbide, A High Temperature Semiconductor," edited by O'Connor, J. R.; Smittens, J., Pergamon Press, N. Y., 1959.
3. HARVEY, C. E., *Research Investigations of Semiconductor Impurities*, "First Quarterly Report, U. S. Army Signal Engineering Laboratories," Ft. Monmouth, N. J., 1959.
4. HATMAN, H. M., *App. Spec.*, **12**, 5 (1958).
5. "Methods for Emission Spectrochemical Analysis," ASTM, Philadelphia, 1957, p. 94.

A. J. MITTELDORF

EXCITATION UNITS

Fundamentals

Any source which is to be used in emission spectroscopy must be capable of (a) introducing the sample into the discharge in a vaporized form, usually dissociated into individual atoms, and (b) exciting the electrons (or the vibrational modes of a molecule) to energy levels higher than the ground state.

Once a sample has been introduced into a discharge and the atoms have been excited to emit light, it can be assumed that: (1) the intensity of a spectral line of an element is proportional to the number of atoms of that element in the sample; and (2) the blackness of a photographed spectral line, or the current from a detector behind an exit slit set on the line is proportional to the intensity of the line in the source and hence

to the concentration of the element in the sample.

Unfortunately, in most cases neither of these assumptions is correct to the degree required for quantitative results good to 1 or 2% precision. Some of the problems associated with condition (1) are discussed below. Condition (2) may not be satisfied simply because of erratic illumination of the spectrograph from exposure to exposure, or because of the complications of photographic photometry.

Gerlach and Schweitzer¹ suggested that safer assumptions would be: (1) the ratio of the intensity of a spectral line of a minor element to the intensity of a spectral line of the matrix element (or an element added in known amount) is a measure of the concentration of the minor element; and (2) the relative blackness of two photographed lines (or the ratio of currents from photomultipliers) can be reduced to the ratio of intensities in the source and hence to the concentration.

Usually it is possible to control conditions so that these two assumptions are justified to within 1%. The resulting analytical procedure is called the "internal standard method" of analysis.

A spectroscopic source unit which is to be used for quantitative spectrochemical analysis must, therefore, either burn off the sample and excite the atoms so reproducibly that a direct measurement of blackness suffices for a measurement of the concentration, or it must burn off and excite the impurity and internal standard elements so similarly that the intensity ratio of their lines will be exactly proportional to concentration.

Introducing the Sample Into the Discharge. A common mechanism for introducing the sample into the discharge is by direct vaporization as a result of the heating of the sample, first perhaps by the electrical current which passes through it as a DC arc is struck, but mainly as a result of the dis-

charge itself. A sample may also be blasted into the discharge as a result of the bombardment of positive ions or possibly high velocity electrons, as in the high voltage spark.²

Vaporization of the Sample. The direct current arc relies almost exclusively on the heating of the sample to volatilize the elements into the arc stream. This results in a process known as *fractional distillation*. During the first few seconds of a discharge such elements as Hg, Cd, Zn, Pb, As, and Sb will vaporize. Then elements such as the alkalis and the transition elements will boil off. Finally the heavy metals, or elements such as the alkaline earths, if present as highly refractory oxides, will begin to appear in the arc stream. The temperature of the discharge will tend to remain constant until each fraction is volatilized. Fig. 1 shows how fractional distillation may be employed in the carrier distillation method for determining impurities in zirconium.

The DC arc is used in several different procedures for semi-quantitative spectrochemical analysis, where the objective is to obtain a quantitative estimate of the concentration of elements in a wide variety of unknowns, accurate to perhaps 25% of the amount present. It is customary to "burn the sample to completion". Unless the unknowns are quite similar, a buffer must be added to establish the volatilization rate and excitation conditions. In such a procedure, the over-all integrated intensity of a line is taken as a direct measure of an element's concentration in the sample.

For accurate quantitative analysis, as mentioned above, it is usually necessary to measure the intensity ratio of two lines, one originating in the standard. Fractional distillation renders this procedure more susceptible to error.

It is easy to see that fractional distillation (Fig. 1) would make it impossible to employ zirconium as an internal standard for the determination of Pb, for example, or to compare elements even more similar in their

Zirconium Oxide with 15% Ag Cl

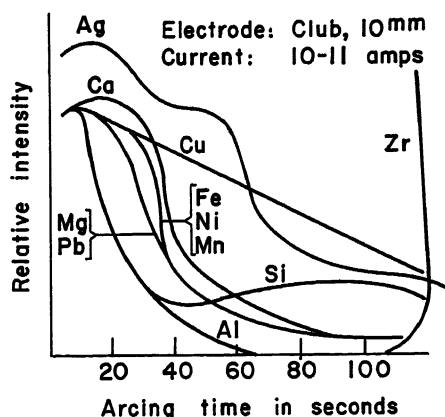


FIG. 1. Fractional distillation in a DC arc.

volatilization rates. Zirconium is obviously so refractory that it does not have a compatible burning time with most of the other elements.

Fractional distillation is present in all cases where the sample becomes really hot, even in the case of a spark, and its effects should always be determined and either offset or corrected.

Ion Bombardment. In the spark, the sample is introduced into the gap primarily by the bombardment of the cathode by energetic positive ions, in the first fraction of a microsecond, when the potential drop across the electrodes is in the thousands of volts. The actual mechanism is not known clearly, but may be due to very high heating, to 10,000 or 20,000° K, in the surface layer of the cathode. In any case, the amount of material volatilized is much less but far more reproducible than in the arc, and with low inductance, there is also very little inter-element effect. If the sample is fine-grained and uniform, with a reproducible surface finish, the rate of sample introduction from exposure to exposure will be highly repeatable. Segregation within the sample, or a coarse and variable grain structure, will introduce variations.

Exciting the Sample. Mechanism of Ex-

citation. Once the atoms of a sample have been introduced to the discharge they may be excited to higher energy levels by: (a) collisions with high velocity electrons or ions; (b) collisions with atoms or ions which have previously been excited, so that during the collision they may transmit some of their energy ("collisions of the second kind"); (c) absorption of radiation emitted by another atom.

All three of these processes are normally active in spectroscopic sources. As the temperature of the source is increased, the kinetic energies of the various particles become higher, so that collisions result in excitation of the higher energy levels. A Bunsen flame at 1600° C will excite only the resonance lines of Na, K, and other elements whose lowest energy levels are less than 2.5 electron volts. The oxy-acetylene flame at 2800° C will excite atomic or molecular band lines for some thirty of the elements with energy levels below about 3.5 electron volts. Arcs at 4500–8000° C emit lines both from the neutral atom and from singly ionized atoms, as do sparks with effective temperatures up to 9000°. High voltage sparks in vacuum produce lines of multiply-ionized atoms.

Effect of Temperature on Excitation. What-

TABLE 1

Source Temperature	Source Temp. Variation ΔT (°K)	Permissible Wavenumber Difference Between Two Lines
2000	10	2800 cm^{-1}
	100	290
	1000	42
5000	10	7000
	100	730
	1000	104
10000	10	14000
	100	1460
	1000	210

These data are calculated for maximum of 1% variation in the line intensity ratio.

ever the mechanism of excitation, the intensity of a spectral line arising from an initial level E_1 is determined by the number of atoms which occupy that energy level, given by:

$$N = CN_{0e} - \left(\frac{E_1 - E_0}{kT} \right)$$

where N_0 is the total density level of atoms, E_0 is the ground state, k is the Boltzmann constant, and T is the effective temperature of the source.

Norris⁸ has pointed out the influence of temperature on the intensity ratio of two lines. If the temperature increases from T_2 to T_1 , there will be a change in intensity ratio of:

$$\frac{\Delta I}{I} = e^{-\frac{h\sigma\Delta\sigma}{k}} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where $\Delta\sigma$ is a given wavenumber separation between the two lines.

Norris presents the data of Table 1 to show the maximum wavenumber difference permissible if the intensity ratio is not to change by more than 1% for specific temperature variations at different temperature levels. As a practical illustration, if Li at 6707 Å is used as an internal standard for the determination of Na at 5890 Å in a flame at 2000°K, the wavenumber separation of 2050 cm^{-1} requires that the temperature not vary by more than 15° to avoid errors in intensity ratios greater than 1%.

Norris emphasizes also the effect of temperature on the degree of ionization. To illustrate, if we attempt to determine Al in a steel using iron as an internal standard, in a source operating at 8000°K, Al will be 42% ionized and Fe only 12%. If the temperature should change to 9000°K, Al would be 67% ionized, Fe 24%. The degree of ionization for the iron would have altered so much more rapidly than aluminum that the intensity ratio would have been changed by 51%.

Self-Reversal. At higher concentrations,

the intensity of a line may be reduced by self-reversal, or self-absorption. In the core of a DC arc, the atoms are traveling at high speeds, some toward, some away from the slit. This introduces a Doppler broadening of the line. In the outer layers of the arc, the temperature is lower and the atoms are traveling more slowly. Outer atoms absorb light traveling toward the slit, which they re-emit in all directions. The net result is a reduction in the light at the very center of the line. Such *self-reversal*, if significant, will considerably reduce the densitometer reading at the peak of a spectral line.

Broadening of Lines. Doppler broadening in the DC arc and Stark broadening in the spark impose limits on resolving power independent of the spectrograph, as mentioned under the discussion of resolution. Isotope analysis may require the use of special cool discharges to sharpen the lines emitted in the source.

Selection of Analytical Line Pairs and Internal Standard. On the basis of the foregoing description and the practical necessities of an analytical problem it is possible to establish the following criteria for selecting an internal standard and suitable analytical lines, as follows:

(a) the internal standard should volatilize approximately simultaneously with the elements to be determined;

(b) the ionization potentials of internal standard and unknown elements should be closely similar;

(c) the lines employed should have closely the same excitation potentials, and should be closely matched in wavelength. They should be free of self-reversal (at least in photographic work);

(d) the internal standard element must either predominate and have relatively the same composition in all samples or it must be introduced as an added element in exactly known concentrations;

(e) if added, the internal standard must not be present in any of the samples in

amounts greater than 1% of the amount added, and the internal standard must not contain impurities at a level that would affect the analytical results.

Excitation Circuits

Direct Current Arc. The DC arc (Fig. 2) is both the simplest and most versatile of spectroscopic sources. The only components required are a direct current power supply, a variable resistor and the discharge gap itself. The arc gap has a negative coefficient of resistance, that is, its resistance falls as the current increases. Accordingly, it is inherently unstable. A relatively high terminal voltage, 150 volts or higher, permits the use of a stabilizing ballast resistor. The voltage across the analytical gap itself will be 20-25 volts when alkali metals are in the gap, and 50-70 volts between carbon or graphite electrodes.

The traditional DC power supply was a motor generator set. However, a full-wave vacuum tube rectifier supply, with a variable core reactor for current control, is now almost universal. Usually currents are between 3 and 10 amperes; when a sample is highly refractory, currents may be increased to as high as 30 amperes. Poritsky⁴ has employed as much as 200 amperes for the analysis of impurities in tungsten.

Some 72 of the natural elements can be determined in the DC arc, in virtually any form of sample. The arc is one of the most sensitive means of excitation, because so much sample is consumed and excited. The line to background ratio is good. If analytical and internal standard lines are carefully

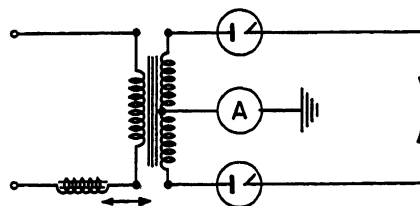


FIG. 2. Circuit diagram for DC arc.

chosen, coefficients of variation as low as 2 or 3% can be achieved. More normal precision is 5–15%.

When the sample is a powder, the usual practice is to insert it in a cavity in the lower electrode, which is made positive. The electrons hitting the anode heat it white-hot, so that the sample is rapidly vaporized.

The Carbon Arc Cathode Layer. Strock⁵ has pointed out that if carbon electrodes are employed and the lower sample electrode is made negative, the specimen will still be vaporized quickly, because of the much poorer thermal conductivity of carbon compared to graphite. Further, there is a concentration of ions (and of neutral atoms after recombination) in a narrow region next to the cathode. Strock achieved greater sensitivities by a factor of 10- to 50-fold when he focused this region of the gap on the slit. The enhancement effect varies from element to element and line to line.

Commercial direct current arcs delivering up to 60 amperes in the most powerful models are produced by Jarrell-Ash Company, National Spectrographic Laboratories, and Baird-Atomic.

The High Voltage Alternating-Current Spark. For routine quantitative results, precise to 1% or better, the high voltage AC spark has proved most suitable. By contrast with the DC arc, the spark has relatively poor concentrational sensitivity, primarily because of relatively high background radiation.

Several different forms of spark are described later, but all have the same basic form of secondary circuit (Fig. 3) consisting

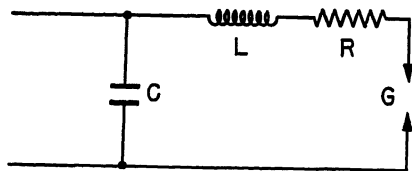


FIG. 3. Secondary circuit of a high voltage spark.

of a high voltage capacitor, C , an inductance, L , a resistance, R , and the gap, G . The various forms of circuit differ mainly in the mechanism used to trigger the breakdown of the analytical gap. In some circuits the gap may break down several times during each half cycle of the primary current supply. At each breakdown, a train of oscillatory discharges passes through the analytical gap, with a frequency determined by

$$f = \frac{1}{2\pi} \sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}},$$

which reduces to

$$\frac{1}{2\pi} \sqrt{\frac{1}{LC}},$$

since R^2 is invariably much less than $4L/C$. The current is given by:

$$i = V \sqrt{\frac{C}{L}} e^{-R/2L} \sin \frac{1}{\sqrt{LC}} t.$$

From this equation it will be seen that the current is increased by increasing V or C or reducing L . Raising the resistance, R , increases the damping. Conversely, adding to the inductance, L , reduces the damping. Finally, increasing L or C decreases the frequency.

The instantaneous voltage across the gap at breakdown will be several thousand volts, but will fall within a microsecond or less to 35–70 volts, corresponding to the DC arc. The initial voltage of the second and later oscillations rises to only several hundred volts. The current in the train of oscillations also falls rapidly if the damping is severe.

Recent studies by Dieke⁶ and Bardocz⁷ have demonstrated that the light emitted during the first 5 to 10 microseconds consists primarily of continuous background and gaseous band spectra. This radiation dies out rapidly, while the emission of the metallic spark lines continues for 40 or 50 microseconds and some arc lines persist for 100 microseconds. As a result, after 10 microseconds the metallic lines stand out relatively clear of

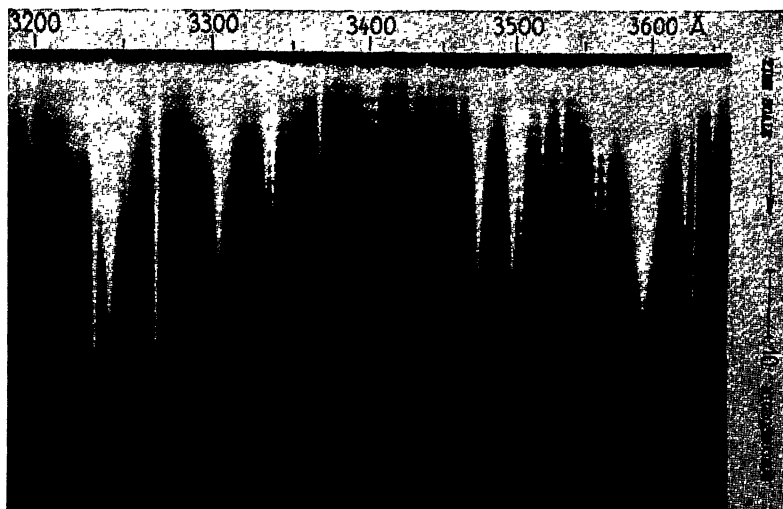


FIG. 4. Time-resolved photograph of a high voltage spark.

background. The effect is shown in Fig. 4 which Bardocz photographed by employing his electronic source and timing mechanism, described later. The individual oscillations, lasting about 2 microseconds, show up clearly.

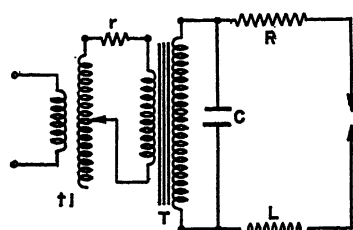
Such time-resolved photographs are valuable for the information they contribute about the physical processes taking place in the spark. If the equipment is arranged to block the first 10 microseconds of each gap breakdown, it is possible to maintain the line intensity essentially unchanged, while markedly reducing the background, thus improving the sensitivity of detection. A comparable improvement in line to background radiation can be obtained by increasing the inductance, which similarly suppresses air lines. Unfortunately, both procedures seem at the same time to reduce the precision slightly. Moreover, increased inductance makes inter-element effects more pronounced.

The Simple Condensed Spark. The earlier circuits (Fig. 5a) employed $\frac{1}{4}$ to 1 K.W. transformers of 15,000 volt secondary. The secondary circuit consisted of a capacitor of approximately .005 μ f, inductance up to

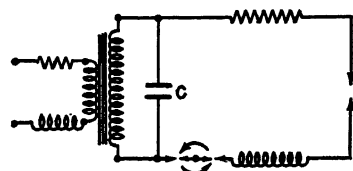
100 μ h, and the analytical gap itself. The secondary voltage could be adjusted by an auto-transformer, and the spark gap might be set at 2, $2\frac{1}{2}$, or 3 mm. The function of the capacitor is to store energy so that when the analytical gap breaks down there will be a large current flow. The larger the current, the brighter will be the lines of metallic elements. The inductance, on the other hand, reduces the instantaneous current flow, which has the effect of suppressing air lines, as pointed out above. The transformer has to have sufficient power to charge the condenser to the voltage required to break down the gap, at least once during a half cycle. Since sharply pointed electrodes in dry air require about 12,000 volts/cm to initiate a discharge, a 3-mm gap between relatively blunt electrodes will require 6000–7000 volts. The power requirement is then given by:

$P = CV_0^2 f$, where $C = .005 \mu$ f, $V_0 = 7000$, and $f = 120$ breaks/second for a 60-cycle current breaking down once each half cycle. This works out to only about 30 watts.

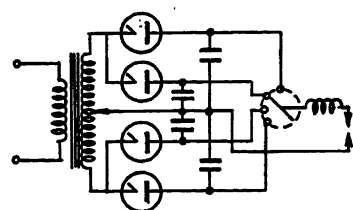
If the resistance in the secondary is minimal—1 ohm or so—an oscillatory train of discharges will take place, with a fre-



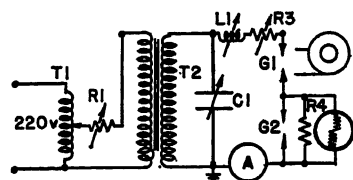
(a)



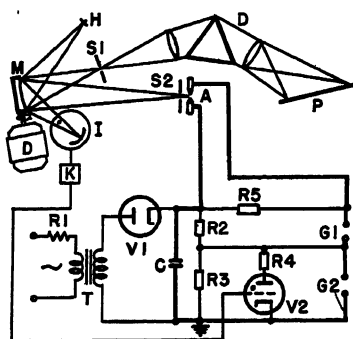
(b)



(c)



(d)



(e)

FIG. 5. Circuit diagrams of common high voltage spark sources.

- (a) Simple condensed spark
- (b) Feussner rotating auxiliary gap
- (c) ARL rotating auxiliary gap
- (d) Michigan auxiliary air gap
- (e) Bardocz electronically ignited spark

quency given by:

$$f = \frac{1}{2\pi\sqrt{LC}} = \frac{1}{2\pi\sqrt{10^{-4} \cdot 5 \times 10^{-9}}} = 2.2 \times 10^6 \text{ oscillations/second}$$

The simple condensed spark is a considerable improvement over the DC arc for general precision, but the gap may not break down each time at the same voltage due to gradual oxidation of the sample and to convection currents across the gap. The duration of the oscillatory discharge also varies with convection currents. For this reason, more elaborate circuits have been developed.

The Rotating Auxiliary Gap or Feussner Spark. In the Feussner circuit (Fig. 5b) the analytical gap cannot break down until an auxiliary rotating electrode comes abreast a fixed electrode. If, at the instant of alignment, the capacitor has reached the required voltage, the whole circuit will break down. The discharge will be quenched rapidly as the auxiliary electrode continues to rotate. Such a circuit, with a synchronous motor, gives highly repeatable times of breakdown and quenching, independent of variations in the conditions at the analytical gap. If the mains supply is constant, or if a voltage regulator is employed, the voltage at breakdown will be repeatable.

A Feussner-type spark was used by Applied Research Laboratories in its original high voltage spark. The principle of the rotary gap was utilized in the Multisource (described later under ignited arcs). The latter forms the basis for the design of the spark section of the ARL High Precision Source. In this, a transformer with center-tap grounded, producing 20,000 volts either side of ground, charges four .007 mfd condensers, two during each half cycle, through rectifier tubes. The condensers are discharged successively by the rotating auxiliary gap (Fig. 5c). The inductance is variable from residual to 1440 microhenries. The auxiliary gap is irradiated by ultraviolet

light from a mercury lamp, to provide a constant level of ions and thus improve the regularity of ignition.

The Auxiliary Air Gap or University of Michigan Spark. In an effort to devise a more direct control over the breakdown voltage, and a simpler mechanical arrangement than the rotating gap, Wolfe and Enns⁹ of the University of Michigan devised a circuit in which the controlling element is a fixed auxiliary gap quenched by an air blast (Fig. 5d). The air blast, at several pounds pressure, quenches each spark train and drives out all ions, so that as the capacitor is charged once more it faces each time an identical condition for breakdown of the gap.

Leeds & Northrup first produced the University of Michigan spark circuit commercially, followed by National Spectrographic Laboratories, Jarrell-Ash Company, and Baird-Atomic. Jarrell-Ash Company, finding that oxidation of the auxiliary electrodes considerably altered the cold emission of electrodes required to initiate the breakdown if no residual ions are present, introduced ultraviolet irradiation of the gap to provide a continuing and constant concentration of ions. The gap then is highly reproducible in voltage, and the need to redress the electrodes is reduced.

A large Jarrell Ash "Varisource" spark unit uses a 7.5 K.W. transformer with 33,000 volt secondary, secondary capacitance up to .015 μ f, inductance up to 1500 μ h and secondary resistance from residual to 3 ohms. The blower for the air blast is mounted internally within the unit. With such a unit, currents as high as 30 rf amperes can be obtained. Also, by reducing the spacing of the gaps, as many as 15 to 25 breakdowns/half cycle can be obtained. This has the effect of spreading the discharge over a wider surface of the specimen, an advantage in some cases of segregation.

National Spectrographic Laboratories and Baird-Atomic produce closely comparable spark circuits.

Electronically Ignited Sparks. For many years it has been recognized that electronic ignition should insure uniformity of breakdown of the analytical gap. However, the ability to handle such high voltages and instantaneous high currents is beyond the capacity of inexpensive tubes. Accordingly, circuits such as those developed by Malpica and Berry¹⁰ suffered from lack of power. It remained for Bardocz¹¹ to solve the problem by the circuit shown in Fig. 5e, which utilizes twin auxiliary spark gaps, G_1 , G_2 . In this arrangement the thyatron tube, V_2 , is used only for ignition and does not itself carry any of the power discharge.

The power capacitor, C , is charged through the rectifier tube, V_1 . The ignition process is started by applying a positive voltage to the grid of thyatron V_2 , so that the tube fires, applying the full voltage of C across G_1 . G_1 breaks down, applying the voltage of C across R_5 and R_4 . R_5 is larger than R_4 , so that the analytical gap, A , breaks down. Now essentially the full voltage of C is applied across R_4 , which breaks down G_2 . C now discharges through the circuit formed by the three gaps, so that V_2 does not have to carry the power.

With this form of circuit, Bardocz has been able to initiate the analytical gap breakdown reproducibly to within a microsecond. By arranging to have the triggering pulse arise from an auxiliary lamp and synchronous rotating mirror (Fig. 5e) Bardocz has been able to sweep the light across the slit of the spectrograph vertically so that the top of the slit is illuminated only by the first microsecond of each breakdown. The rotating mirror then records a time scale down along the slit. Fig. 4 was photographed in this way. By mounting a rotating sector in front of the slit and arranging to have it initiate the triggering pulse five to ten microseconds before the slit is exposed, it is possible to obtain spectra free from the air lines and continuous background emitted in the first phase of the oscillatory discharge.

The Bardocz circuit is utilized by Metrim-pex of Hungary and by Jarrell-Ash Company in their electronically controlled spark source units. According to the evidence available to the author to date, the superior precision of ignition does not improve the analytical accuracy over that of carefully adjusted Feussner- or Michigan-type sparks.

High Voltage AC Arc. Duffendack and Thomson,¹² in 1936, applied a high voltage AC arc to the analysis of caustic liquors. They obtained even better sensitivities than in a DC arc, with considerably better reproducibility. The same source has since been applied to the analysis of other solutions or powders, which are dried or applied to the flat ends of both graphite electrodes. The high voltage AC arc has been used also to detect trace elements in metals, below the limit of detection of the spark, with greater precision than a DC arc.

The circuit is shown in Fig. 6. The transformer has a split secondary winding, so that the two halves can be put in series to give approximately 5000 volts, or in parallel for greater current, up to 5 amperes, at approximately 2500 volts. The current control is usually by means of a variable reactance.

With alkali salts as sample, the AC arc is usually self-sustaining for a gap of $\frac{1}{2}$ to 1 mm, even at 2500 volts. The 5000 volt discharge is self-sustaining for metal samples. In either case, the gap breaks down as the voltage approaches its peak in each half cycle. The voltage then drops rapidly to 25–80 volts and an arc-like discharge occurs until the voltage starts to reverse, when the arc is terminated, to be re-ignited on the next half cycle.

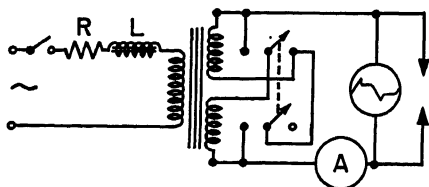


FIG. 6. High voltage AC arc circuit diagram.

The radiation comes mainly from the arc-like phase of the cycle so that the spectrum has low background. The re-ignition each half cycle at a new and randomly selected part of the specimen provides better sampling than a DC arc. The high reactance provides a relatively stable discharge. Accordingly, the source has excellent sensitivity and fair reproducibility. Unfortunately the high-voltage AC arc is dangerous enough to cause fatalities.

Interrupted Arcs. Several different ignited arc circuits have been developed in the hope that it would be possible to attain the reproducibility of the high-voltage spark without sacrificing the sensitivity of the DC arc. The aim is to ensure that the discharge initiates at random spots over the sample surface as contrasted to the DC arc, where the cathode spot migrates erratically around the surface as determined by convection currents and oxidation of the material. With random ignition, the effects of fractional distillation and irregular sampling should be reduced. If a large amount of material can still be vaporized and excited, and if the radiation of continuous background and gaseous lines can be minimized, a superior source should be achieved. Unfortunately, except in rare instances, ignited arcs of all forms seem to give reproducibility slightly inferior to a high-voltage spark and sensitivity not quite as good as the DC arc. However, such results may be more appropriate to a particular analysis.

Mechanically Interrupted Arcs. A DC arc may be interrupted by drawing the electrodes apart rapidly, or by opening the circuit through a relay, and it can be re-ignited by touching the electrodes. Such arrangements are achieved by a specially constructed arc stand, rather than by any special circuitry.

The Pfeilsticker Arc. Pfeilsticker¹³ used a high-frequency Tesla discharge to break down the analytical gap, and a brush contacting metallic segments in an insulating

rotating disc to interrupt the arc. Pfeilsticker's original circuit is shown in Fig. 7. The transformer $Tr(J)$ charges the condenser, C_1 , until the gap, F , breaks down. Through the Tesla transformer, T , a high-frequency current is induced in the main circuit. The voltage across C_2 , .0004 μf , rises very rapidly, to break down the analytical gap, B . The rotating disc, U , terminates the discharge after 5 to 50 milliseconds. L_1 , L_2 , and C_2 act as a filter circuit to block the high frequency from the mains. The current is controlled by the variable resistor, W , and is read on the ammeter, A .

Later Pfeilsticker¹⁴ improved the circuit by increasing C_2 to 50–100 μf . Then the interrupter can be emitted because, as soon as C_2 discharges, it short-circuits the gap, thereby terminating the discharge.

The *ARL Multisource*. Hasler and Dietert¹⁵ developed a circuit (Fig. 8) in which a

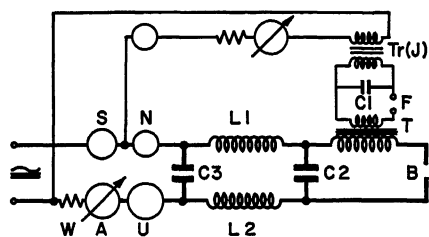


Fig. 7. Pfeilsticker ignited AC arc.

variable capacitor is charged through a rectifier during one half cycle and then is discharged through the analytical gap during the next half cycle. The discharge through the gap is initiated by a low power high voltage spark, controlled by a rotating synchronous gap. The main power circuit consists of the half wave rectifier, surge suppressor, capacitor bank variable from 2 to 62 μf , inductance up to 360 μh , resistance from residual to 200 ohms, the analytical gap, and the monitoring oscilloscope. The triggering circuit includes a half wave rectifier, capacitor, rotating synchronous gap with ultraviolet irradiation, and the analytical gap. The transformer of the power circuit develops 850 volts, while the transformer of the spark circuit is adjustable up to 20,000 volts.

With full capacitance and inductance the frequency approaches 1000 cycles/second and the individual oscillations last for several milliseconds—an arc-like condition. Residual inductance and reduced capacitance produce a higher frequency, with shorter duration oscillations, more like a high voltage spark. Adding resistance increases the damping to the point where only a single oscillation occurs.

The Multisource has been applied to a wide variety of analytical work, and in

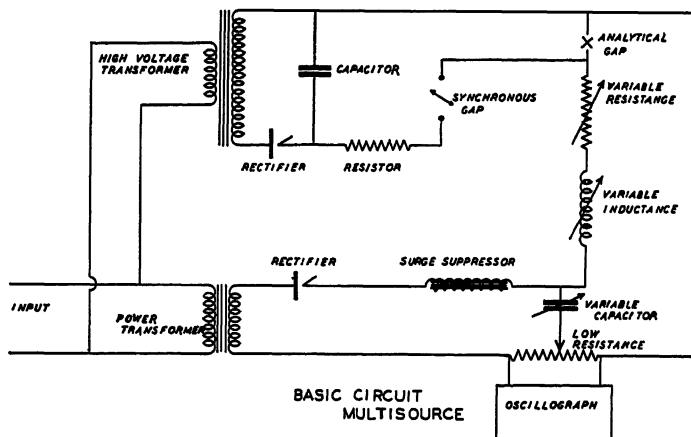


Fig. 8. Multisource ignited arc source unit.

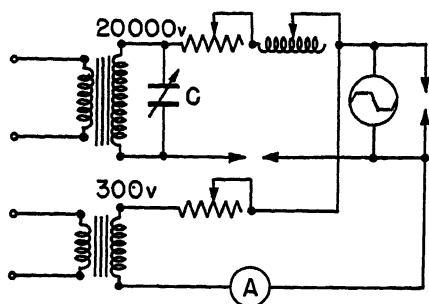


FIG. 9. Spark-ignited AC arc circuit.

general has approximately the sensitivity of the DC arc with a precision approaching that of the spark.

Spark Ignited AC Arcs. A low voltage AC supply, at 230 to 600 volts, can be made to support a discharge by re-igniting the arc at each half cycle by means of a high voltage spark or Tesla coil. A typical circuit is shown in Fig. 9. The triggering spark is initiated by a rotating interrupter (Applied Research Laboratories), auxiliary air gap (National Spectrographic Laboratories, Jarrell-Ash Company), point discharge gap (Hilger & Watts), or electronic pulse (Bardocz-Metrimex).

The low voltage supply can be half-wave or full-wave rectified, to produce a uni-directional discharge (uni-arc).

The power of the spark is usually kept low, so that the major radiation comes from the arc discharge, when high sensitivity is desired. However, by increasing the relative power of the spark, it is possible to obtain greater precision with slightly reduced sensitivity. The ignited arcs yield analytically the same results as the high-voltage AC arc, and have largely replaced the latter, since they are less dangerous and they are inexpensive to add to a high voltage spark source.

High Resolution Sources. For most spectrographic problems the instrumental and source resolution obtained is entirely adequate. However, two highly important areas of investigation have been limited by

the lack of resolution in the source. These are wavelength standards and isotopic analysis.

Line broadening is produced by Doppler effects, pressure interactions, and the Stark effect. Doppler broadening is the principal cause of lack of resolution and it is most likely to occur in arc sources. Unfortunately, the high sensitivity and ability of the arc source to excite refractory and electrically non-conductive materials make it most likely to be used for isotopic work or exciting wavelength standards.

Two sources have been developed to overcome the Doppler broadening effect. They are the hollow cathode and the radiofrequency excited sample.

Hollow Cathode. In 1926, Shüler¹⁶ described a cooled hollow cathode source which gave extremely narrow lines, but it was not until the development of the AEC program for isotopic analysis and the production of isotopes that emphasis was given to the use of this source in isotopic investigations. The hollow cathode has a number of advantages in this application, however. It has high sensitivity, re-uses the sample, and entirely encloses radioactive and/or toxic materials.

McNally and his co-workers¹⁷ at Oak Ridge have reported on the use of the hollow cathode source for the analysis of the isotopes of lithium. The Li 6707 Å line investigated for the $\text{Li}^6\text{-Li}^7$ isotopic shift shows extreme Doppler broadening. It was impossible to overcome this by the instrumental resolution of the spectrograph and, therefore, the hollow cathode excitation provided a convenient answer to the problem.

Radiofrequency Source. In the search for better primary wavelength standards, Meggers used the electrodeless discharge tube excited by a diathermy unit. By pile irradiation of Au^{197} , Hg^{198} can be produced. This material is extremely valuable as a source for a primary wavelength standard and, therefore, a small amount of it is sealed in a low pressure discharge tube and excited

with a 100 megacycle RF unit. Meggers and Kessler¹⁸ of the National Bureau of Standards have reported on this application.

REFERENCES

1. GERLACH, W. AND SCHWEITZER, E., "Foundations and Methods of Chemical Analysis by the Emission Spectrum," London, Adam Hilger, Ltd., (1934).
2. KAISER, H. AND WALLRAFF, A., *Ann. Physik*, **34**, 297 (1939).
3. NORRIS, J. A., "Excitation Theory in Spectrochemical Analysis," Unpublished Paper Presented at the Fall Meeting of the Southeastern Association of Spectrographers, Oak Ridge, Tennessee (1953).
4. PORITSKY, A., Gen. Elect. Co., Cleveland Wire Works, Cleveland, Ohio. No published work.
5. STROCK, L. W., "Spectrum Analysis with the Carbon Arc Cathode Layer," Adam Hilger, Ltd., London (1936).
6. CROSSWHITE, H. M., STEINHAUS, A. W., AND DIEKE, G. H., *J. Opt. Soc. Am.*, **41**, 299 (1951); **43**, 257 (1953).
7. BARDOZ, V. A. AND VARSANYI, F., *Z. Naturforsch.*, **10A**, 1031 (1955).
8. FEUSSNER, O., *Arch. f. Eisenhüttenwesen*, **6**, 551 (1932).
9. ENNS, J. H. AND WOLFE, R. A., *J. Opt. Soc. Am.*, **39**, 298 (1949).
10. MALPICA, J. T. M. AND BERRY, T. M., *Gen. Electric Rev.*, **44**, 563 (1941).
11. BARDOZ, V. A., *Appl. Spectroscopy*, **11**, 167 (1957).
12. DUFFENDACK, O. S. AND THOMSON, K. B., *Proc. A.S.T.M.*, **36**, II, 301 (1936).
13. PFEILSTICKER, K., *Zeitsch. Electrochem.*, **43**, 719 (1937).
14. PFEILSTICKER, K., *Zeitsch. Metallkunde*, **30**, 211 (1938).
15. HASLER, M. F. AND DIETERT, H. W., *J. Opt. Soc. Am.*, **31**, 140 (1943).
16. SHÜLER, H., *Z. Physik*, **35**, 323 (1926).
17. STUKENBROEKER, G. L., SMITH, D. D., WERNER, G. K., AND McNALLY, J. R., JR., *J. Opt. Soc. Am.*, **42**, 383 (1952).
18. MEGGERS, W. F. AND KESSLER, K. G., *J. Opt. Soc. Am.*, **40**, 737 (1950).

R. F. JARRELL

FLUORIDE EVOLUTION METHOD

Fluoride compounds have been used in spectroscopy both as stable compounds and

unstable compounds. The former class is represented by the fluorides of barium, strontium, and lanthanum, and the latter by the fluorides of copper and uranium.

The stable fluorides have been used both as matrix compounds and as additives with graphite to promote smoother burning of refractory oxides such as zirconium oxide and tantalum oxide. The exact electrode reactions have not yet been established, but it is theorized that there may be formation of fluorides after reduction of the oxide by the graphite. The stable fluorides volatilize smoothly and with a minimum tendency for eruptive gas emission.

The unstable fluorides have been used essentially as specific reagents for the determination of boron and silicon in oxides of a variety of materials. While the reaction of uranium fluoride is the same as that of copper fluoride, the copper fluoride is more practical from the standpoint of availability and simple spectrum. Copper fluoride is either loaded into the bottom of the electrode crater to be followed by the sample or mixed with the sample prior to loading the crater. Upon heating, the copper fluoride decomposes to free fluorine which sweeps the boron and silicon into the arc column where they can be excited essentially free of matrix. This separation permits determination of boron and silicon with a minimum interference from other elements. In practice the procedure has been found to be useful with a wide range of arc currents, electrode types, and sample sizes. The most precise work has been obtained using a boiler cap to reduce arc wandering and matrix excitation to a minimum. The copper fluoride evolution technique for boron and silicon has been applied to steels, refractory oxides, graphite, bismuth, nickel, and other materials. By varying the sample size and arc current determinations of boron have been made over a concentration range of 0.1 ppm to 3,000 ppm.

J. E. PATERSON

GASES IN METALS

Several techniques for the spectrographic determination of the gaseous elements have been suggested. The most successful technique is based on extracting the gaseous elements with a d-c carbon arc discharge and then exciting the emission spectra of the extracted gases with the same discharge. The basic steps involved are shown in highly schematic form in Figure 1. The metal samples, in which the gaseous element impurities are represented as dissolved oxides, nitrides, and hydrides, are supported in specially designed carbon electrodes. These electrodes form the anode of d-c arc discharges in argon at atmospheric pressure. If electrodes of this type are designed properly, the arc discharge quickly melts the metal specimen. The molten sample then dissolves the retaining wall of the electrode and forms a globule supported on the floor of the electrode. The dissolved carbon comes into intimate contact with the dissolved oxides, nitrides, and hydrides, causing chemical reduction reactions as shown in Equation 1. Simultaneously, a saturated solution of carbon in the metal is formed, which reduces the volatility of the metal.

The rate and degree of evolution of the

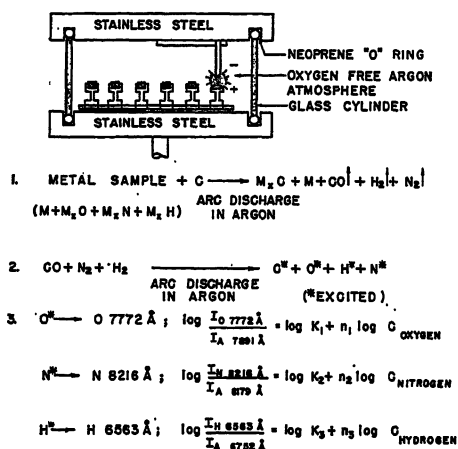


FIG. 1. Processes involved in the spectrographic determination of oxygen, nitrogen, and hydrogen in metals.

oxygen, nitrogen, and hydrogen contents are critically dependent on the environmental conditions in the graphite supporting electrode. For reproducible quantitative evolution, the electrode wall should be completely dissolved, so that the arc rests directly on the globule. The temperature of the anode spot is then equal to the boiling point of the globule material ($\sim 3500^\circ\text{C}$), whereas the temperature in the remainder of the globule undergoes a precipitous gradient to about 1500°C at the electrode-melt interface. The high localized temperature and efficient convection stirring induced by the high temperature gradient both contribute to fast reaction rates and rapid gas evolution.

Since the gas evolution reactions proceed somewhat erratically, it is desirable to allow them to reach completion before starting the spectroscopic exposures. The evolved gases are then determined as impurities in the supporting argon atmosphere.

As shown in Figure 1, a d-c carbon arc discharge in argon dissociates the molecular impurities and excites the atomic emission spectra as the molecules undergo natural diffusion through the arc column. The lower part of the figure shows how the intensity ratios of selected oxygen, nitrogen, hydrogen, and argon line pairs are related to the impurity concentration in the sample. The selected argon lines serve as almost ideal internal standards under these excitation conditions, especially for the determination of oxygen and nitrogen.

The main experimental difficulty associated with this technique is the contamination of the purified argon atmosphere with oxygen, nitrogen, hydrogen or their compounds liberated from the walls of the excitation chamber or from the supporting electrodes during the excitation cycle. This source of error can be reduced to tolerable proportions by careful design of the excitation chamber and thorough out-gassing of the electrodes and chamber. If argon gas of sufficient purity is not available, the oxygen

and nitrogen content may be reduced to acceptable limits by employing a purification system.¹

The excitation chamber consists of two water-cooled stainless steel plates separated by a glass cylinder (Figure 2). Neoprene or rubber O rings resting in grooves are used to obtain airtight seals. Four C clamps placed symmetrically around the chamber apply pressure to the plates to assure airtightness. Each excitation is performed in a static atmosphere of purified argon at atmospheric pressure. A stainless steel rotating platform with iron (magnetic) inserts accommodates 12 sample electrodes and one auxiliary outgassing electrode. The platform can be rotated from outside the chamber by a permanent magnet. The counter electrode is stationary and can be used for 20 or 30 exposures without replacement.

Prior to use, each of the 12 electrodes is outgassed by arcing at 35 amperes under a reduced argon pressure for 5 seconds, and then the chamber is evacuated while the arc is continued for another 10 seconds. After loading the sample electrodes, the inside surfaces of the chamber and the electrode surfaces are outgassed by operating a 30 ampere arc discharge to the auxiliary cylindrical electrode for 3 minutes with water-cooling of the O ring cavities only. Two outgassing arcings are made, with intervening evacuation and replenishment with pure argon. When the samples are excited, the water-cooling cavities are flushed with cold water. After the excitation cycle for each sample is completed, the chamber is evacuated, a new charge of argon is admitted while a new sample is rotated into position.

The exact dimensions of the electrode used for the simultaneous determination of oxygen and nitrogen in low and high alloy steels are shown in Figure 3. The arcing cycle consists of a 2-minute pre-arc at 25 amperes during which the gases are evolved, followed by a 2-minute exposure. Because some high alloy steels contain rather high

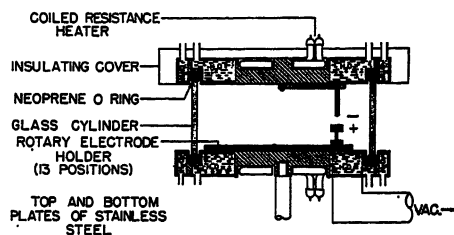
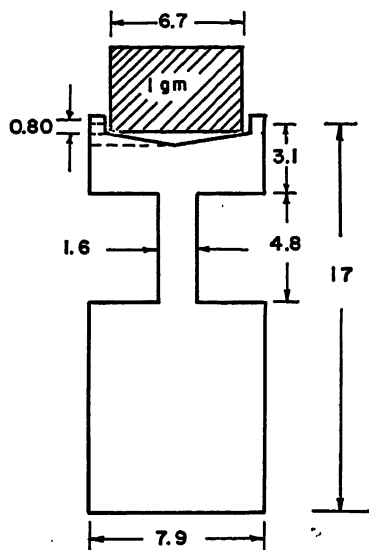


Fig. 2. Schematic diagram of excitation chamber.



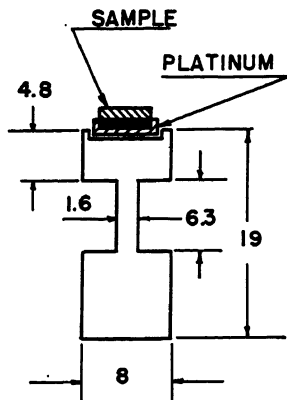
DIMENSIONS ARE IN MILLIMETERS

Fig. 3. Electrode dimensions for the determination of oxygen and nitrogen in steels.

percentages of relatively volatile manganese, it is desirable to conduct the spectrographic exposure by arcing to the auxiliary electrode. The auxiliary electrode is rotated into position after the gas extraction phase is completed. The analytical curves established for the determination of oxygen and nitrogen in low and high alloy steels cover the range 0.002 to 0.2 weight per cent for oxygen and 0.01 to 0.5 weight per cent nitrogen. No matrix effects have been observed for the rather wide range of alloy compositions studied. Preliminary experiments indicate that the oxygen content of vanadium, nickel, and copper metals can be determined in this manner. The rate and degree of evolution of

the oxygen content of these metals are critically dependent upon electrode geometry.

The simple expedient of arcing metal specimens of zirconium, titanium, thorium, etc., in graphite electrodes does not cause reproducible evolution of the oxygen content. This problem has been solved by employing an electrode assembly which provides a molten platinum bath after the arc is initiated. In essence, the platinum bath provides a reaction medium in which the gas evolution re-



DIMENSIONS IN MILLIMETERS

Fig. 4. Electrode assembly for the determination of oxygen in titanium and other refractory metals.

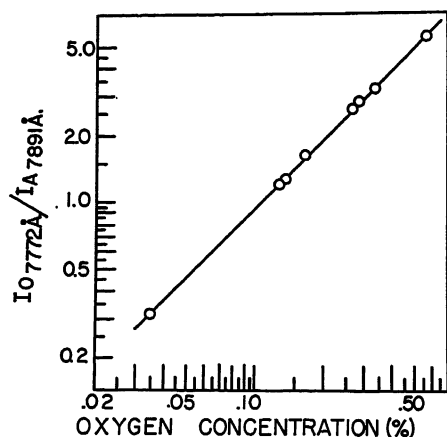


Fig. 5. Analytical curve for the determination of oxygen in titanium and titanium alloys. Concentrations are expressed in weight per cent.

actions proceed rapidly and reproducibly. For most metal systems it is necessary to assure complete alloy formation between the sample and platinum before any of the metal sample reacts with the graphite electrode. The electrode assembly designed especially for this purpose is shown in Figure 4. The metal specimen weighing 100 mg is pressed into a platinum wafer weighing 500 mg. Care must be taken that the platinum wafer provides a physical barrier between the metal specimens and the graphite supporting electrodes. These electrode assemblies are arced at 15 amperes for 10 seconds. During this period a violent alloying reaction occurs, producing a bright flash. After 15 seconds, the arcing current is increased to 30 amperes to assure maximum bath temperature and temperature gradient. The evolution of the oxygen content is virtually complete in about 30 seconds, after which time the oxygen/argon intensity ratio stabilizes. Spectrographic exposures are made during the 30 to 60 second period.

The analytical curve for the determination of oxygen in titanium and titanium alloys is shown in Figure 5. This curve has been used directly for the determination of oxygen in zirconium metal. Similar curves have been obtained for the determination of oxygen in niobium and yttrium metals.

Studies on the determination of hydrogen have revealed that the hydrogen line at 6563 Å is readily detectable when 200 mg specimens of titanium containing hydrogen are arced in graphite electrodes at 30 amperes. The behavior of the hydrogen/argon intensity ratios during the arcing cycle indicates that the hydrogen is evolved rapidly—during the first 10 seconds—and then appears to be removed from the system as the arcing proceeds, probably through chemisorption. A marked enhancement of the hydrogen line intensity occurs as the arcing cycle is conducted at lower pressures. Although maximum hydrogen line intensities are observed at pressures less than 100 mm

of Hg, it is desirable to compromise the advantages of maximum hydrogen line intensities with the disadvantages of increased metal volatilization at these low pressures. For quantitative determinations, an argon pressure of 125 mm of mercury, an arcing current of 30 amperes, and exposures during the 10 to 40 second period are used.

REFERENCES

1. FASSEL, V. A. AND TABELING, R. W., *Spectrochim. Acta*, **8**, 201 (1956).
2. FASSEL, V. A. AND GORDON, W. A., *Anal. Chem.*, **30**, 179 (1958).

V. A. FASSEL

GRATINGS, PRODUCTION OF

The ruling of a high-quality, large diffraction grating requires a mechanical precision equaled in few other fields of human endeavor. The aim for a grating of 30,000 grooves/inch is to rule the last groove of a 6" or 8" grating with a tolerance of ± 0.0000003 " with respect to the first groove. Furthermore, the individual grooves should be held within the range 7000–8000 microns wide, and each should be tilted at a definite "blaze" angle, with respect to the original surface, usually in the range 3° to 15° , to within a few tenths of a degree. All grooves should be accurately parallel. The depth of the rulings should be the same, and should be free particularly from "chatter" of the ruling diamond. Figure 1 shows a magnified view of what a grating should be, with tolerances indicated. It is easy to see why a perfect grating has never been produced, and why there are so few successful ruling engines.

The art of ruling high-quality gratings was first developed by H. A. Rowland,¹ and all successful engines still employ his basic principles; most of them derive from the ruling operations which he initiated at Johns Hopkins University in 1882, as shown in the family tree for ruling engines in Figure 2. Successful ruling ventures usually involve a

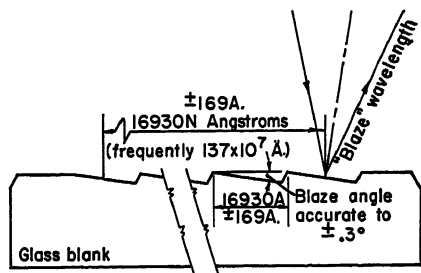


FIG. 1. Enlarged cross section of a grating of 15,000 grooves/inch.

scientist as leader and a highly skilled, painstaking and patient machinist as operator. This article describes three different forms of ruling engine, but it should be emphasized that the output of a successful ruling engine will depend fully as much on the skill of the operator in diagnosing and correcting its continual minor, and occasional major, maladies, as on the original soundness of design and care in construction. Grating ruling is still very much an art. The three successful basic designs known to the author are the original Rowland construction, sketched in Figure 3a, the Strong² arrangement (Fig. 3b), and the interferometrically controlled engine of Harrison.³

The Rowland Design. In the Rowland design, the grating blank sits on a table which is moved on straight ways by a precision screw and nut, typically thirty threads to the inch. On one end of the screw is mounted an accurately cut dividing head, with say 1000 teeth. If a pawl or other indexing mechanism moves the dividing head one tooth, the grating table will advance $1/30,000$ ", provided that the screw itself is constrained from moving and the nut is prevented from rotating. The screw is supported at each end in bearings and is maintained precisely in position either by a hardened steel ball contacting a diamond mounted on the end of the screw opposite the dividing head, or by a "zero pitch thread," i.e., annular grooves cut in the screw ends and in the bearings. The nut is kept from

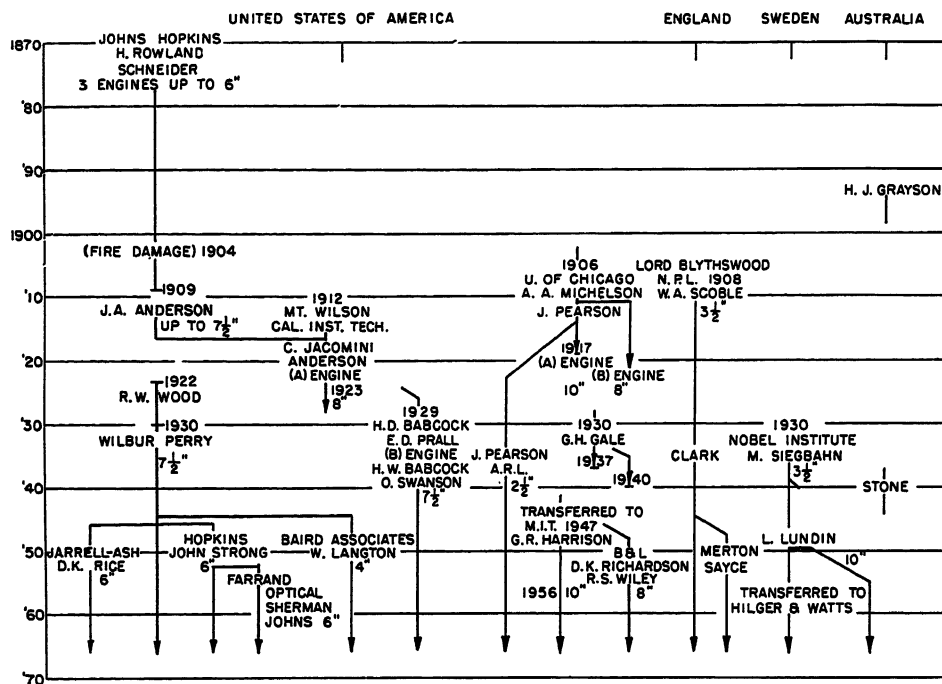
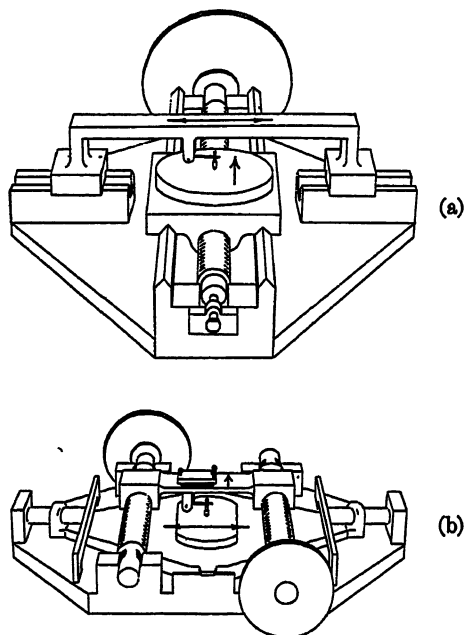


FIG. 2. A family tree of the grating ruling art.

FIG. 3. Two basic designs of mechanical ruling engine. (a) Rowland; (b) Strong. (Courtesy *Journal of The Optical Society of America*)

rotating by a "tail" riding against a "liner bar" set parallel to the grating ways.

The ruling diamond is mounted on a carriage moved by a reciprocating drive on ways at right angles to the main ways. As the grating is being advanced, the diamond is raised from the surface. Then as the indexing mechanism is returning for the next stroke, the diamond is lowered and rules a groove.

The Strong Design. In Strong's design (Fig. 3b) the grating spacing is derived by advancing the ruling diamond, which is mounted on a carriage moved by one right-handed and one left-handed screw. The two screws are simultaneously indexed. The ruling is produced by a reciprocating motion of the table which bears the grating blank. Fundamentally, compared to machine tools, the Rowland design corresponds to a shaper, while the Strong engine is similar to a planer.

In the Strong arrangement all grooves

must be parallel to one another unless the grating ways wear significantly during a ruling, whereas in the Rowland design parallelism of the grooves depends on the straightness of the grating ways. This is an important advantage, because "fanning" of the grooves destroys resolution.

Spacing Errors. These two mechanical engines are susceptible to the same errors in spacing, of which the most significant are:

(1) A sudden break in the spacing, so that one area of the ruling is out of phase with the rest. Several such errors result in a multiplicity of spectral lines. The trouble is normally traced to a slippage of some critical part of the ruling engine.

(2) Erratic spacing of individual lines about an average spacing that is well maintained. Such random errors result in "grass" around the spectral lines; a heavily exposed line will show a host of close weak satellites spreading out on both sides. The problem lies in some part of the engine which has a slight amount of play. Frequently the pivot bearings which permit the diamond to be raised and lowered may have such lateral play.

(3) A long-term variation in the spacing of the grooves, so that the wavefront from the grating, in the order being used, shows a "hill" or "valley" departing by more than one-quarter wavelength from a plane wave front. Such variations will produce satellites, the intensity of which depends on the degree of departure from a plane wavefront. The cause is frequently a variation in temperature greater than $.01^{\circ}\text{C}$, which will expand or contract the screw; or it may be faulty lubrication of the screw or ways or inadequate "pre-run."

(4) "Error of run," a gradual increase or decrease of the spacing across the grating, so that the emergent wavefront will be concave or convex, but cylindrical to within $\frac{1}{4}\lambda$. Such an effect imparts a variable focus to the grating, so that the focal curve is not strictly the Rowland circle if concave, or, if

plane, the focus changes with angular rotation of the grating. Improper lubrication, wear of the ways or screws and nut, or a gradual drift in temperature may result in such variations. (Grating blanks which are not truly spherical or plane may introduce a closely similar defect.)

(5) "Periodic errors," a variation of spacing repeated (a) with each complete or integral fractional rotation of the screw, or (b) at regular intervals represented by a beat frequency between two repetitive cycles in the engine. Condition (a) produces the familiar "Rowland ghosts"; condition (b) results in "Lyman ghosts" (see p. 256). Rowland ghosts may result from:

(a) Lack of concentricity between the bearings of the screw and the axis of the helix represented by the thread after final lapping. This produces a drunkenness in the revolution of the screw, which in turn results in a sinusoidal variation in the spacings.

(b) Failure to prevent the screw from moving slightly forward and back as it is rotated. If the steel ball is mounted slightly off center and the thrust diamond is not mounted exactly at right angles, the screw will weave in and out as it is rotated. A like effect is obtained if the zero pitch threads depart at all from planarity. Again, a sinusoidal variation in spacing results.

(c) Errors in the dividing head or eccentricity in its mounting. The dividing head is most frequently the source of the higher-order ghosts; a fourth-order ghost, spaced four times as far from the parent line as the first ghost, may result from a variation in the spacing of teeth on the dividing head, which is repeated four times in one revolution.

An examination of the accuracies which it would be necessary to achieve in each of these errors, at several levels of Rowland ghost intensity, is given in Table 1. From these data it would seem that it should be a fairly straightforward, if painstaking, matter to achieve a ghost intensity of $1/25,000$. In practice, a first-order ghost intensity below

EMISSION SPECTROSCOPY—LIGHT

TABLE 1. PRECISION OF PARTS REQUIRED TO PRODUCE LOW ROWLAND GHOSTS 15,000 Grooves/Inch

Ghosts Below	1/1000	1/10,000	1/25,000	Precision Achievable
Over-all Periodic Error in microns	.0169	.0054	.0034	
in ten millionths inch	6.7	2.1	1.35	
Spacing Wheel (500 teeth, 7" radius)				
Corresponding Accuracy of Dividing, in Seconds	26	8.25	5.2	3
Corresponding Accuracy of Centration, in ten thousandths of an Inch	16.4	5.2	3.6	1.0
Thrust Bearing (Flatness Assumed $\frac{1}{10}$ Fringe)				
Perpendicularity in Seconds of Arc	2	2	2	1
Corresponding Centration, mm	1.7	.5	.34	.1
Screw and Nut Periodic Error	Contributes negligible problems for a well-lapped screw.			
Concentricity of Bearings	$\frac{1}{2}$ fringe Hg green is sufficient and is achievable.			
Pitch Diameter	May produce error of run, but no periodic error.			
Linkage, Nut to Table	Produces no periodic error.			

1/1000 for a grating of 15,000 grooves/inch is considered satisfactory, and ghost intensities less than 1/4000 are exceptional. Actually, a part of the art of a grating ruling machine operator consists in his ability to determine the sources of periodic error and either to correct them or to offset one against the others.

Lyman ghosts were introduced in one of the Johns Hopkins engines inadvertently, when the driving belt for the whole unit had a fastener which introduced a disturbance

approximately every five grooves. The effect was eliminated by substituting a continuous belt and by introducing a form of shock-absorbing spring balance wheel. In modern engines, where adequate care has been exercised to avoid a possible coincidence of repetitive errors, Lyman ghosts are usually at a very low level, below 1/50,000, and introduce no serious problems.

Interferometrically Controlled Engine. Since 1950, G. R. Harrison at Massachusetts Institute of Technology has been perfecting the ruling of gratings with interferometric control. Initial attempts to utilize interferometer fringes as a means of arresting the grating carriage precisely proved disappointing when applied to the normal start-stop system of ruling. Far better results were achieved when the diamond and ruling carriage were continuously moved, and the interferometer fringes were employed to maintain a regular relationship in the X, Y coordinates. The system employed is shown in block diagram form in Figure 4

A DC motor is operated at constant speed by a flywheel and electronic feedback, through a 100:1 gear reduction. This motor turns a shaft which drives the diamond carriage through a linkage mechanism (designated "rectifier" in the figure) which converts the normal simple harmonic motion into a linear motion during the ruling stroke. The same shaft actuates a reference signal generator which produces a sinusoidal current, adjustable in phase to correct for atmospheric pressure changes. The shaft also advances the grating carriage, through a change gear system which controls the spacing, and a differential and worm and large worm gear mounted on the screw. A Michelson-type interferometer, with reference plates secured to the ruling engine frame, and with the traveling plate mounted on the grating carriage, produces moving fringes which generate a sinusoidal current from a photomultiplier as the carriage moves uniformly along. The amplitudes of the reference and photomultiplier signals are meas-

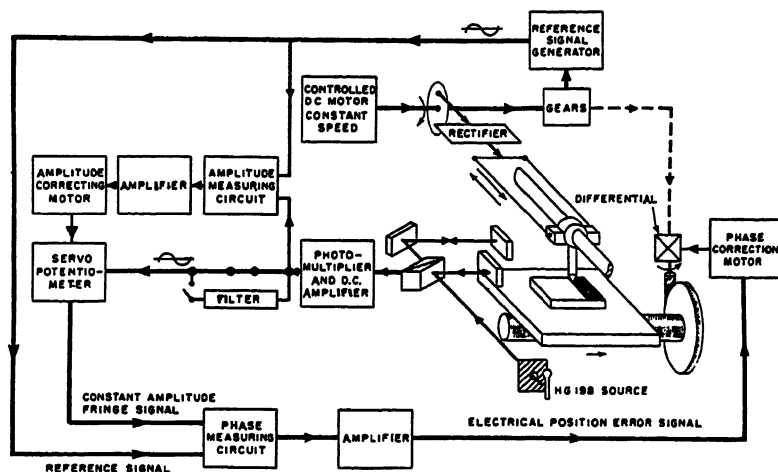


FIG. 4. Block diagram of Harrison interferometrically controlled ruling engine. (Courtesy *Journal of The Optical Society of America*)

ured and automatically equalized. The relative phase of the two signals then actuates a servo motor which drives the differential device, to either advance or slow the grating carriage to maintain synchronism between diamond and grating blank, with a precision of a few hundredths of a fringe of Hg 5461 Å.

Harrison has demonstrated that with interferometric control it is possible to reduce Rowland ghost intensities to less than 1/20,000 (first order, 15,000 grooves/inch) and to maintain the over-all precision of spacing over a ruling width up to 10". Several large gratings ruled on the Harrison engine surpass any grating previously produced, achieving resolving powers approximating one million.

Intensity Distribution. The grooves of a grating are produced by a diamond point and the action may be likened to that of a plow cutting a furrow in the ground, in the sense that material is not cut and removed from the grating blank, but rather that the surface is deformed. The objective, however, is to produce a smooth groove, shaped at the desired angle, with uniform depth. Two forms of diamond are usually employed, as shown in Figures 5a and 5b. Form (a) is better suited to concave gratings; form (b)

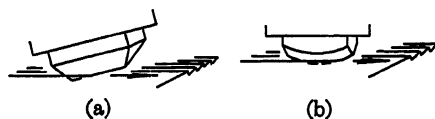


FIG. 5. Two forms of diamond used in grating ruling. (a) Straight edge; (b) "Cance" shaped.

is more rugged but the groove angle is more difficult to control.

Gratings for many years were ruled in speculum metal, but then the process of evaporating aluminum on chromium on glass, and later aluminum directly on glass, was developed successfully. The aluminum surfaces are not only superior for reflectivity, but are adequately adhesive and far easier to rule. Silver and copper have also been tried for infrared gratings. The grating blank is normally a glass with low temperature coefficient of expansion. Occasionally fused quartz is employed, to reduce temperature effects still further.

The depth of the ruling is determined by the hardness of the surface which is being ruled and by the weight added above the diamond, beyond that required to obtain a balance. To reproduce results from ruling to ruling it is necessary to maintain the same hardness in aluminized or other reflecting

surfaces. If too heavy a weight is employed, the groove produced may considerably exceed the desired spacing. In this case, each new groove will seriously deform the previous groove, completely changing the groove angle and leaving an irregular surface which will yield an unexpected intensity distribution in the final grating. On the other hand, too light a ruling will produce an inefficient grating, with high intensity in the central image. The optimum groove seems to be about 85–95 % of the spacing. This yields a minimum of deformation of the desired groove angle by the succeeding ruling, yet utilizes essentially the entire surface.

If one face of a diamond is set to produce the desired low order blaze, the included angle of the diamond determines approximately the blaze on the other side of the grating normal. Thus, for example a grating blazed for 10° , ruled by a diamond of 120° included angle, may have a high intensity on the other side at 50° . However, the steep side of the groove is most distorted by the

ruling of the next groove, so that practice seldom follows theory closely in this respect.

Replication of Gratings. For many years replicas of gratings have been produced quite simply by flowing a thin coating of collodion over the grating surface, allowing it to harden, and then stripping the replica off the surface. The process has been refined further by floating off the collodion by immersing the coated grating in water, and then bringing a replica blank up under the separated collodion film. This avoids severe strains and distortions, but nevertheless replicas so produced do not begin to compare in quality with the grating from which they were taken. They are suitable for applications where a high aperture ratio is the prime requirement, and definition and scattered light are relatively unimportant.

A process introduced by Fraser and White⁴ yields far superior results. Figure 6 diagrams the process. The master grating is placed in a vacuum coating vessel and a thin "parting layer" of a greasy substance is deposited on it (17 in the figure). Then a layer of Al 1500–2000 Å thick is evaporated onto it (18). The coated master is removed from the vacuum and covered with a thin layer of plastic (19), and this is covered by the replica blank (20). After 24 to 48 hours, polymerization of the plastic will be complete and the master and the replica may be separated at the parting layer. The parting layer is then washed off. If the process has been adequately controlled, spectra from the replica and master will be indistinguishable.

It has been claimed that replicas obtained by this process are actually superior to the master. The author is unable to subscribe to this theory. It is true, however, that a current replica grating is quite likely to be superior to the average original ruling of several years ago, not only because the ruling art has improved, but also because the manufacturer can now afford to select as masters only superior rulings, rejecting

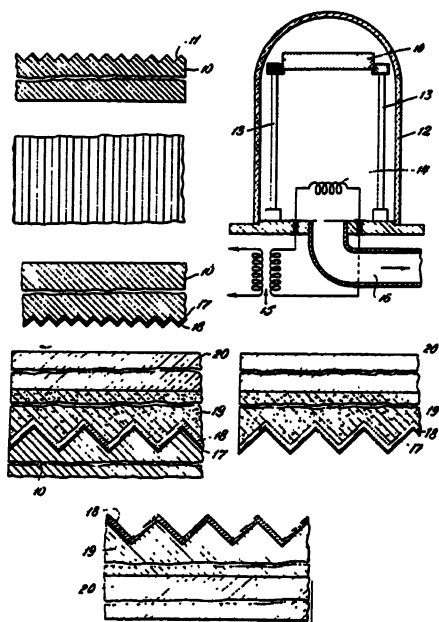


FIG. 6. Replication procedure. (Courtesy Perkins-Elmer Corporation)

marginal or even average gratings which formerly would have had to be used.

Merton Gratings. Merton⁵ has suggested that a relatively inferior screw produced on one end of a highly polished cylindrical rod could be employed to generate a highly precise screw on the other end of the cylinder. On the original thread is mounted a nut consisting of an outer metallic shell and an inner lining of cork. Such a nut, if prevented from turning, will advance smoothly and steadily, as the screw is rotated, without periodic or random errors, which will be averaged out by the elasticity of the cork.

If a diamond point is attached to an arm extending out ahead of the nut, and if the pitch is made as fine as 1/2000" to 1/7500", a cylindrical grating, free of errors, can be ruled on the far end of the rod.

Since a cylindrical grating is not useful in itself, it is necessary to produce replicas from this master. This is done by forming around the cylinder an intermediate pellicle, which is then slit and spread out into a flat. The replicated grooves of the pellicle are then impressed in a plane gelatine blank. The gelatine is hardened and aluminized, to form the final replica grating.

The Merton process has been developed to a high art by Sayce⁶ and co-workers at the National Physical Laboratory in England, and is used by Hilger Watts, Ltd., and Paton Hawksley to produce gratings for the infrared or for instructional purposes. However, the complexities of the replication technique are so great that it has not been possible to produce gratings of the quality required for emission work in the visible and ultraviolet.

REFERENCES

1. ROWLAND, H. A., *Phil. Mag.*, **13**, 469 (1882).
2. STRONG, JOHN, *J. Opt. Soc. Am.*, **40**, 455 (1950).
3. HARRISON, G. R. AND STROKE, G. W., *J. Opt. Soc. Am.*, **45**, 2, 112-121 (1955).
4. FRASER, W. AND WHITE, J., U.S. patent 2,484,738.

5. MERTON, T. R., *Proc. Roy. Soc.*, **A201**, 187 (1950).

6. SAYCE, L. A., *Spectrochimica Acta*, **6**, 57 (1953).

R. F. JARRELL

GRATING SPECTROGRAPHS AND SPECTROMETERS

Advantages of Plane Gratings. When in 1882 and 1883 Rowland¹ demonstrated theoretically that a concave reflection grating would function if the rulings were spaced equidistantly on the chord, so that it became feasible to fabricate such a device, and when he and his machinist, Schneider, indeed succeeded in producing an excellent example, all interested scientists adopted this new tool with enthusiasm. From 1883 to 1950 concave gratings reigned supreme. Although plane reflection gratings were somewhat simpler to generate (and the difficulty of ruling an adequate supply of gratings for many years limited their application), they were employed infrequently, usually for high resolution research work. The commercial grating spectrographs developed from 1935 on all utilized concave gratings. During the last decade the tide has flowed strongly in the opposite direction, until today only one manufacturer retains the concave grating in a large photographic spectrograph for the usual analytical range. Concave grating instruments are still employed in the vacuum ultraviolet or for fixed position spectrographs. The plane grating spectrographs have become important for a number of reasons. From the point of view of the operator they are the following:

(1) Adjustment of wavelength range is much simpler.

(2) Higher orders can be reached, for higher dispersion and resolution.

(3) Most of the plane grating designs are highly stigmatic.

(4) The instruments tend to be more compact.

From the point of view of the manufacturer they are:

(1) The mechanical adjustments are simpler.

2. The plane gratings can be ruled, replicated and tested more readily and their intensity distribution more precisely controlled.

Plane Gratings instead of Prisms

In many cases plane gratings can be substituted for prisms in the mountings previously described. For example, it has been common practice to use plane reflection gratings in constant deviation spectrometers. Long 40-foot Littrow plane grating spectrographs have been built by R. W. Wood and others for very high-resolution work. There are practical difficulties, however. If a plane grating is substituted for a prism in a commercial large Littrow quartz spectrograph, the tilt of the plateholder will be so much less that the range of adjustment available will not suffice.



FIG. 1. Original Ebert plane grating spectrograph, designed in 1889.

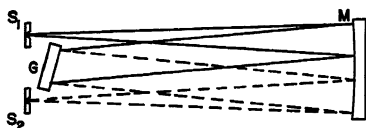


FIG. 2. Fastie plane grating scanning spectrometer.

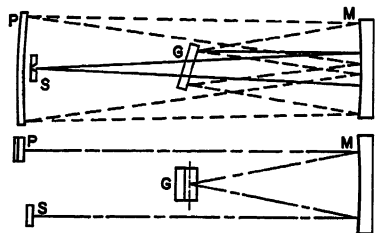


FIG. 3. Fastie modified "over-under" Ebert spectrograph.

Plane Grating Spectrographs

The Ebert Mounting. In 1889 Ebert² advocated the mounting shown in Fig. 1. The design was criticized by Kayser and was never adopted generally. In 1952 William G. Fastie³ independently developed the same basic design for a high resolution scanning spectrometer (Fig. 2). Fastie's work and enthusiasm stimulated interest in the original Ebert arrangement, which may be designated a "side-by-side" design. The entrant rays are on one side of the grating; the emergent rays on the other. Fastie suggested a modification, an "under-over" design (Fig. 3). The entrant rays pass below the grating while the emergent rays pass above.

The Ebert mounting is achromatic, as indeed is any plane grating design which utilizes concave mirrors rather than lenses as focusing elements. This results from the separation of the image-forming and dispersing elements. It is possible to change the wavelength range merely by rotating the grating—a major advantage. On the other hand, as indicated in the diagram, while the rays returned by the grating to the mirror are parallel for any given wavelength, the rays for different wavelengths are divergent. Hence a large objective mirror is required to cover any extended wavelength range at the camera. Fastie suggested that the grating be moved at least halfway toward the concave mirror, so that a relatively smaller mirror will encompass a wide wavelength range.

Jarrell-Ash Company has utilized the Fastie Ebert under-over design in 3.4-meter and 2.5-meter plane grating spectrographs (Fig. 4). The grating is rotated by a worm gear and worm drive operated from the front of the spectrograph, with either a counter to read the angle, or a wavelength scale. In the 3.4-meter model a large grating ruled with 15,000 grooves/inch over $5\frac{3}{8}'' \times 2\frac{1}{4}''$ gives a first-order dispersion of 5 Å/mm over a range of 2100–4700 Å. A grating of 30,000 grooves/inch yields 2.4 Å/mm. Gratings are

readily interchangeable, to suit unusual applications. A Littrow quartz prism can be substituted for the grating, covering the entire wavelength range from 2100–8000 Å simultaneously, at a dispersion comparable to a large Littrow quartz spectrograph.

Since the grating can be rotated to angles as high as 70° , it is possible to reach wavelengths up to 3 microns with a grating of 15,000 grooves/inch or 6 microns with a grating of 7500 grooves/inch. Thus the 25th order of 2537 Å can be photographed at a dispersion of 0.18 Å/mm, to obtain resolution above 400,000. The coarser grating produces a larger number of overlapping orders, so that a grating of 7500 grooves/inch will cover the complete range 2055 Å–4360 Å without gaps by the 17th through 9th orders at dispersions ranging from 0.50 to 0.95 Å/mm. An "order sorter" is offered to separate out the orders, so that they are recorded simultaneously, one above the other. The order sorter consists of a low-dispersion direct-vision illuminator, with the slit and optical axis horizontal and, therefore, "crossed" with the grating dispersion.

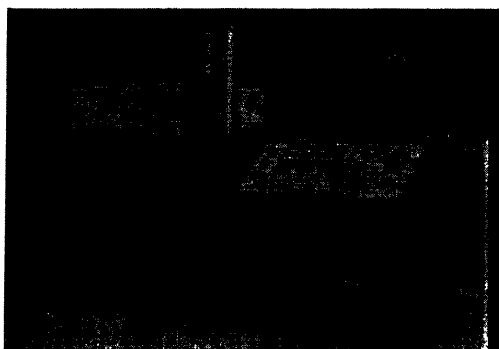
The Jarrell-Ash Ebert Spectrograph (Fig. 4) can be supplied also with a direct reading head on the side, with a large mirror which can be inserted in the optical path at 45° to divert the light. Twenty or more exit slits and photomultipliers can be accommodated. The instrument can be used also as a high-dispersion scanning spectrometer, either by adding a head with a fixed and a scanning exit slit for ratio measurements, or by a slow motion scanning drive for the grating. The Jarrell-Ash design of Ebert spectrograph is manufactured under license by Hilger & Watts, Ltd., in England, and has been copied in Japan by Shimadzu.

Bausch & Lomb Optical Company has utilized the Ebert mounting in its two-meter dual grating spectrograph (Fig. 5). Since the grating is positioned near the slit-camera end of the instrument, the large 18 inch mirror covers a field of only 10 in. To obtain a field of 20 in., two separate gratings

are employed, each covering 10 in. The gratings are independently adjustable. Normally the spectrograph is supplied with a first grating of 30,000 grooves/inch, which is used in the first order at 4 Å/mm, covering 1000 Å, and a second grating of 15,000 grooves/inch, blazed for the second order, to cover another 1000 Å at 4 Å/mm. The second grating may be used also to record the higher wavelengths in the first order at 8 Å/mm, but because of the blaze will be very weak in the low wavelength first order.

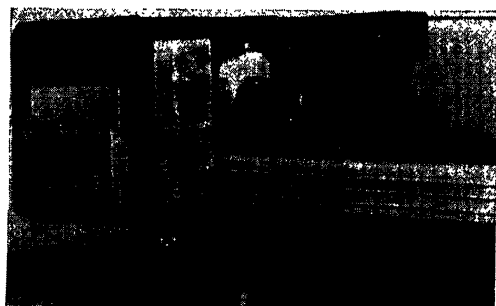
A dual condensing system utilizing a biprism is provided to permit illuminating the two gratings from a single source.

Optica of Milan and Zeiss of Jena are currently introducing Ebert-type plane grating spectrographs.



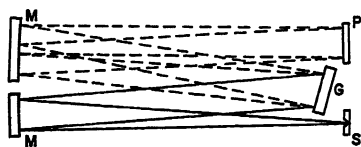
(Courtesy Jarrell-Ash Company)

FIG. 4. Jarrell-Ash Ebert 3.4 meter spectrograph, with direct reading head.

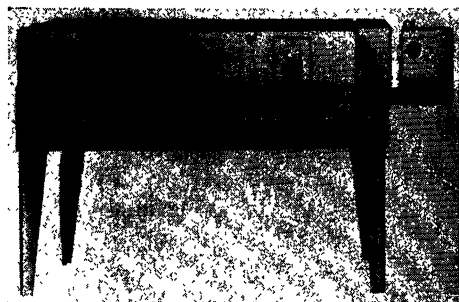


(Courtesy Bausch & Lomb Optical Company)

FIG. 5. Bausch & Lomb 2-meter dual-grating spectrograph.



(a)

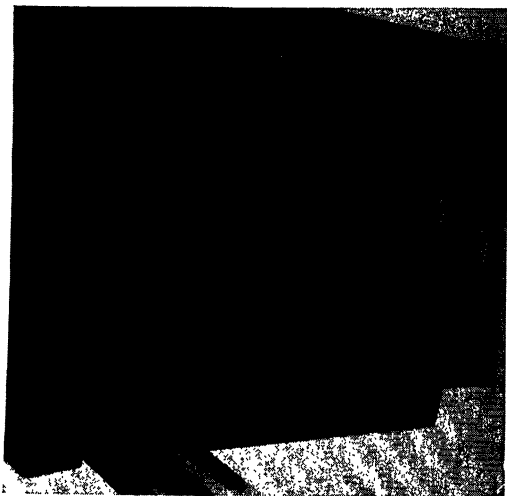


(Courtesy Applied Research Laboratories)

(b)

FIG. 6. Czerny-Turner 1.5 meter spectrograph of Applied Research Laboratories.

Czerny-Turner Mounting. A design similar to Ebert's, but utilizing two concave mirrors in place of the single large mirror, derives from the Czerny-Turner⁴ mounting for monochromators, illustrated in Fig. 6a. This constitutes a more practical way of achieving a



(Courtesy Jarrell-Ash Company)

FIG. 7. Jarrell-Ash high-aperture Czerny-Turner spectrograph.

side-by-side Ebert design for a spectrograph, since the second mirror can be made large to cover an adequate field, whereas a single mirror would have to be so wide as to be impractical.

Applied Research Laboratories has utilized this basic design in its 1.5-meter "Quantograph", shown in Fig. 6b. With a grating of 30,000 grooves/inch a first-order range of about 2000 Å is recorded at 5.6 Å/mm on a 15-in. length of 35-mm film. The spectrograph may be provided also with an array of exit slits and photomultipliers for use as an integrating direct reader, or with a single exit slit and slow motion drive for the grating, for use as a scanning spectrometer.

Jarrell-Ash Company employs a similar design in an F/6.5 plane grating spectrograph, of 750 mm focal length (Fig. 7). (The normal grating spectrographs have aperture ratios in the range F/24 to F/40.) Gratings of 4 × 4-in. ruled area and spacing of 600 or 1200 grooves/mm are interchangeable, giving first-order dispersions of 22 or 11 Å/mm, respectively, over a 7-in. focal field. A 3-ampere iron arc will record a strong spectrum in 1/100 sec. on Eastman SA 1 emulsion.

Several F/1.1 high-aperture plane grating spectrographs have been built by the Naval Gun Factory and Naval Research Laboratory, based on a design of J. G. Meinel, using a corrector plate. This instrument gives excellent speed and definition, suffering only from the inconvenience of a focal curve not exterior to the instrument.

Bass and Kessler⁵ and others have built high-aperture grating spectrographs, utilizing commercial photographic lenses. This is an inexpensive method of achieving speed with good definition, but the glass optics restrict such instruments to the range above 4000 Å.

Concave Grating Spectrographs

Mountings. Once the focusing conditions for the concave grating had been formulated, a series of papers appeared, proposing different mountings for the concave

grating designed to maintain slit, grating and plate- or film-holder on the Rowland circle. The more important are shown in Figs. 8-15.

The *Rowland mounting*⁶ (Fig. 8) utilizes the geometric principle that the locus of the apex of a series of right triangles having a common hypotenuse is a circle having the hypotenuse as a diameter. The grating, *G*, and plateholder, *P*, are fixed on opposite ends of a rigid bar, which forms the hypotenuse and the diameter of the Rowland circle. The slit, *S*, is placed at the intersection of two tracks, *SP* and *SG*, which are carefully constructed at right angles. Rollers under *G* and *P* are constrained to travel along *SG* and *SP*, so that as the bar, *GP*, is moved, the grating remains on the optical axis fixed by the condensing system, and the Rowland circle moves to coincide with all three optical elements.

The principal advantage of the Rowland mounting is that the plated holder remains on the normal to the grating, so that the dispersion is linear over a wide range of wavelengths. For this reason, it was extensively used for early wavelength measurements. However, the more accurate Fabry-Perot etalon is now used for such determinations. The Rowland design is awkward in its mechanical adjustments, bulky, and scarcely susceptible to a self-contained construction. As a result, the mounting has never been successfully employed in a commercial spectrograph and few, if any, of the early two-room forms of Rowland mounting survive, even in academic circles.

The *Paschen-Runge, or Paschen, mounting*⁷ (Fig. 9) has been used more extensively than any other for broad surveys of complex spectra. For such work, large circular tracks

FIG. 8. Rowland.

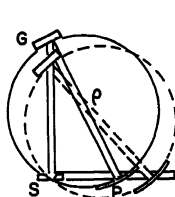


FIG. 9. Paschen-Runge.

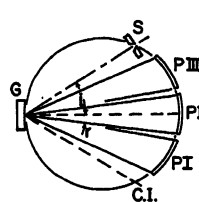


FIG. 10. Abney.

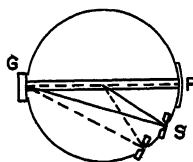


FIG. 11. Eagle.

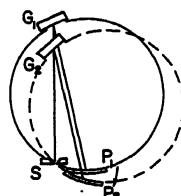


FIG. 12. Radius.

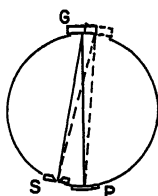


FIG. 13. Wadsworth.

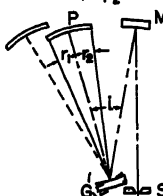


FIG. 14. Seya-Namioka.

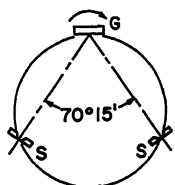
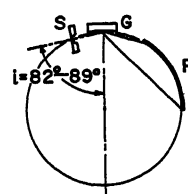


FIG. 15. Grazing incidence.



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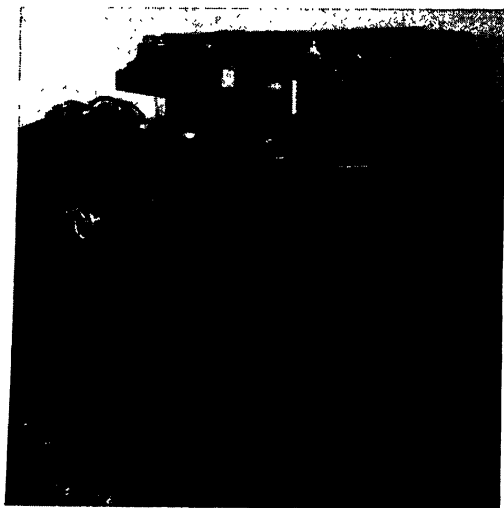
of 21 or 35 foot diameter are built in a room which can be temperature-stabilized and darkened. Plateholders can be clamped to these tracks where desired. The slit mounts protrude through a wall into an adjoining room where the excitation equipment and light sources are located. The advantages of the Paschen mounting are:

(1) After the initial construction it is very simple mechanically.

(2) Plateholders can be clamped to cover an extended wavelength range and several different orders simultaneously.

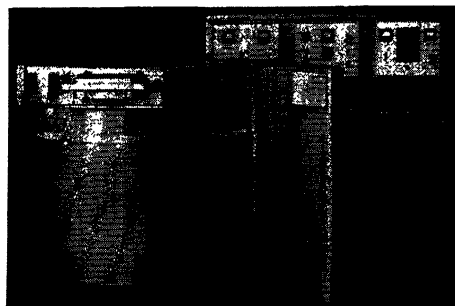
The disadvantage of the mounting is its extreme bulk.

The *Abney mounting*⁸ (Fig. 10) was developed to retain the linear dispersion feature of the Rowland mounting with a simpler mechanical arrangement. The plateholder is mounted on the normal to the grating. The slit is mounted on an arm rotating about the center of the Rowland circle to change the wavelength range. The slit assembly must also be rotated about an axis below the slit opening itself, so that the source-slit axis will still point at the grating. Although the Abney arrangement is somewhat simpler mechanically and more com-



(Courtesy Applied Research Laboratories)

FIG. 16. The 1.5 meter Abney-form spectrograph of Applied Research Laboratories.



(Courtesy Applied Research Laboratories)

FIG. 17. The ARL 2 meter Paschen spectrograph.

pect than the Rowland, it too has been largely abandoned with the shift of research activity from wavelength measurements to high-resolution work over extended wavelength ranges.

Commercially the 1.5-meter and 2-meter spectrographs manufactured by Applied Research Laboratories can be considered as modified forms of Abney or Paschen mountings. These mountings also constitute the basis for the spectrometers of the ARL Quantometers. In the original 1.5-meter spectrograph (Fig. 16) the filmholder was on the normal to the grating and the slit position was moved to pick up the second order. In the 2-meter (Fig. 17) and later 1.5-meter design, the filmholder was moved to change the wavelength range. These ARL spectrographs have been discontinued in favor of plane grating designs. Instruments patterned after the ARL are being produced now by Manufacture Belge de Lampes et de Matériel Électronique S.A. in Brussels and by Shimadzu in Kyoto.

ARL 1.5 meter spectrographs are found throughout the world. The specifications of the original 1.5-meter are typical: A $14\frac{1}{2}$ " length of film covers the range 2150–4370 Å or 4350–6570 Å at 7 Å/mm in the first order, using the standard grating which is ruled with 24,000 grooves/inch over an area of 1×2 in. An alternative grating of 36,000 grooves/inch produces 5 Å/mm. The optical bench in the second slit position can be used to obtain second order spectra.

The *Eagle mounting*⁹ (Fig. 11) is more compact than any other form of concave grating spectrograph. Since the slit and plateholder are close together, the astigmatism is less than in other forms of Rowland circle mounting. Three independent mechanical adjustments are required to maintain the elements on the Rowland circle:

(a) The grating must be rotated to change the wavelength range.

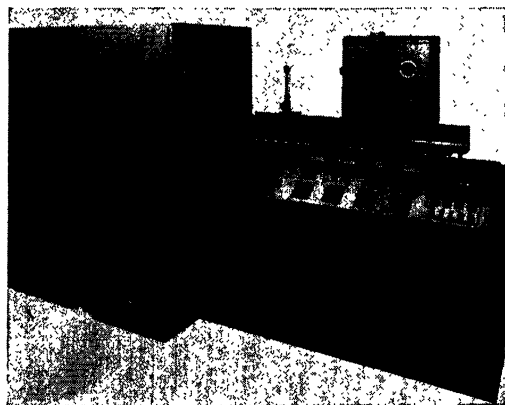
(b) The grating must be moved along the optical axis to maintain the focus.

(c) The plateholder must be tilted about an axis under the slit to remain in focus across its length.

It will be seen that these adjustments are analogous to those required by the Littrow prism spectrograph.

The Eagle mounting is still used extensively, both for special research spectrographs and for commercial instruments. Its compactness renders it particularly suitable for vacuum spectrographs, which have a minimum pumping volume and maximum mechanical strength if they are built as a cylindrical tank.

Commercially the Eagle mounting has been manufactured since 1938 by Baird Associates (now Baird-Atomic) of Cambridge, Massachusetts (Fig. 18). The three adjustments cited above are made by motor



(Courtesy Baird-Atomic, Inc.)

FIG. 18. The Baird-Atomic 3 meter Eagle spectrograph.



(Courtesy Jarrell-Ash Company)

FIG. 19. The Jarrell-Ash 1 meter Eagle vacuum spectrograph.

drives actuated by push buttons until a counter for each indicates the appropriate reading. A table supplied with the instrument shows the appropriate dial settings for several selected wavelength regions. In the low wavelengths, diaphragms, filters or sector discs can be placed at the Sirks' position, so that they are in focus.

The earlier Baird three-meter Eagle spectrograph was supplied with a 10-in. plateholder, which covered a first-order spectral range of about 1400 Å at 5.6 Å/mm, with a grating of 15,000 grooves/inch. Recently the plateholder has been expanded to 20 in.

For its direct-reading spectrometers, Baird-Atomic employs the basic Eagle arrangement also, in the sense that slit and focal curve are adjacent and the incident and emergent angles are as nearly as possible the same. A similar arrangement is used by Jarrell-Ash Company for its vacuum direct reader. Hilger & Watts and Jarrell-Ash Company manufacture Eagle vacuum spectrographs and scanning spectrometers (Fig. 19).

G. R. Harrison pointed out that the relatively small astigmatism of the Eagle mount could be almost wholly corrected by introducing between the slit and grating a low

power cylindrical lens, with axis horizontal. This has the effect of bringing the Sirks' focus into coincidence with the slit, at least for one wavelength. Bausch & Lomb has utilized this principle in its 1.5-meter spectrograph (Fig. 20). This instrument covers 2200–6200 Å at 16 Å/mm on a 10-in. film, or 4500–7000 Å at 10 Å/mm, depending on the grating.

In the *Beutler radius mounting* (Fig. 12), developed at University of Chicago and described by Sawyer,¹⁰ the slit and plateholder are mounted permanently on the Rowland circle, and the grating is mounted on an arm which rotates about the center of the Rowland circle. This arrangement is particularly suited for a vacuum spectrograph or scanning spectrometer, because the slit and plateholder or exit slit can be mounted on the external walls of the vacuum chamber, where they are accessible for adjustment or manipulation. Motion of the grating within the vacuum is readily accomplished, and after the initial adjustment does not need to be accessible. Furthermore, by rotating the grating about a vertical axis under its face, the central image can be brought onto the plateholder or exit slit and used to adjust for focus—always a problem in the vacuum ultraviolet. The disadvantage of the radius mounting is that the grating rotates away from the initial optical axes, so that either the axes must be changed or there is a practical limit to the extent of wavelength adjustment.

The radius mounting has been utilized commercially by Baird-Atomic and by McPherson for a scanning vacuum ultraviolet



(Courtesy Bausch & Lomb Optical Company)

FIG. 20. The Bausch & Lomb 1.5 meter Eagle spectrograph with cylindrical lens.

spectrometer, based on a specific design suggested by Tousey and Watanabe.

Of all mountings for the concave grating, the *Wadsworth*¹⁵ (Fig. 13) is most unusual, in that the focal distance is half the radius of curvature, the individual elements are not located on the Rowland circle, and a second optical element is introduced in the form of a concave collimating mirror. This arrangement produces a stigmatic image and a linear dispersion, as in the Rowland and Abney mountings. The concave mirror is mounted at its focal distance from the slit, tilted slightly off axis to irradiate the grating with parallel light. The grating may be located either side of the optical axis, as close to it as possible to minimize aberrations. The plateholder is located on a bar the axis of which forms the normal to the grating. To change the range to higher wavelengths, the bar is rotated away from the mirror about an axis under the grating face. The plateholder must be moved away from the grating to remain in focus. In any one position of the plateholder the lower wavelengths lie *nearest* to the concave mirror. This appears paradoxical until one realizes that in changing the range it is the angle of incidence which is varied, while at a given setting it is the angle of diffraction that defines the progression of the spectrum.

In a 21-foot Wadsworth spectrograph, designed by the author and manufactured by Jarrell-Ash Company in 1942, the unique advantages of the grating were first utilized in a commercial spectrograph, which was as stigmatic as prism instruments.

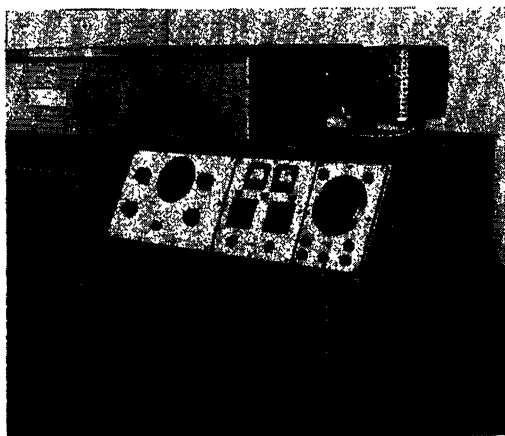
A 6-in. diameter grating ruled with 15,000 grooves/inch over an area of $5\frac{3}{8} \times 2\frac{1}{4}$ in. introduced resolution available previously only in large laboratory-built apparatus. The 5 Å/mm first-order dispersion exceeded that of all other instruments except the large quartz spectrographs in the far ultraviolet (which in turn could be surpassed in the second and third orders), yet the 20-in. plateholder covered in a single setting the entire range from 2100 Å to 4700 Å, to in-

clude the most sensitive lines for all elements except the alkalis. Other notable features were an electromagnetic shutter to time exposures and automatic racking for the plate-holder. The wavelength range, read from a scale, could be changed by a motor drive, with focus automatically maintained. This instrument has been superseded now by a plane grating spectrograph.

Jarrell-Ash Company still manufactures fixed position 1.5-meter Wadsworth spectrographs (Fig. 21). These inexpensive spectrographs record on a 20-in. film either 2100–4800 Å at 5.4 Å/mm with a grating of 30,000 grooves/inch, or 2100–7800 Å at 10.9 Å/mm with a grating of 15,000 grooves/inch.

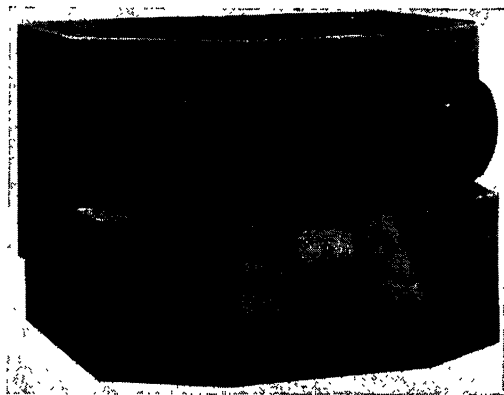
Jarrell-Ash Company employs a "dual deck" Wadsworth mount in its 2.5-meter direct reader, utilizing two collimating mirrors to illuminate a single grating, producing two identical spectra side by side. This makes it possible to set exit slits on adjacent lines, one on each deck, and it provides twice as much space for mounting photomultiplier tubes.

The *Seya-Namioka*¹¹ mounting (Fig. 14) was suggested by M. Seya and T. Namioka in 1952. They pointed out that if the angle between the entrant and emergent rays in a spectrometer was $70^{\circ}15'$ there would be



(Courtesy Jarrell-Ash Company)

FIG. 21. The Jarrell-Ash 1.5 meter Wadsworth stigmatic spectrograph.

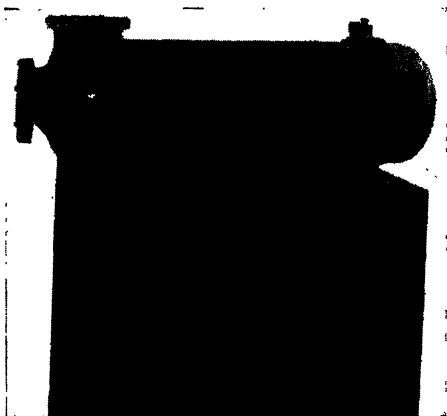


(Courtesy Jarrell-Ash Company)

FIG. 22. Seya-Namioka .5 meter scanning vacuum spectrometer of Jarrell-Ash Company, for the range 500 Å to 3000 Å, extending to 10,000 Å.

such slight defocusing, if the grating was merely rotated about its own vertical axis, that the image would be entirely acceptable for scanning monochromator usage in the vacuum ultraviolet and even into the visible and infrared. The design lends itself ideally to vacuum ultraviolet work, since the entrance and exit slits can remain fixed, as in the Radius mounting, while the mechanical motion for the grating is even simpler. Furthermore, the optical axes remain fixed. Paul McPherson and Jarrell-Ash Company have produced scanning spectrometers for the vacuum ultraviolet, utilizing this design (Fig. 22).

Grazing Incidence. If a grating is illuminated at grazing incidence, the short wavelengths below 1000 Å will be totally reflected, whereas the reflectivity of aluminum or all other known reflectors or coated reflectors falls off rapidly from a maximum of perhaps 20% at 1000 Å to a few per cent at 500 Å. For this reason Hoag¹² in 1927 first experimented with a grazing incidence spectrograph (Fig. 15). Angles of incidence as high as 85° – 89° have been employed to observe wavelengths as low as 53 Å¹³ or even 12.1 Å.¹⁴ The astigmatism of a grating at such high angles becomes extreme, partially offsetting the advantage of total reflection. Dispersion



(Courtesy Jarrell-Ash Company)

FIG. 23. Jarrell-Ash Company 1 meter grazing incidence vacuum spectrograph, for the wavelength range 50 Å–3100 Å.

is good for a one-meter spectrograph with grating of 30,000 grooves/inch, about 3 Å/mm at 1000 Å, and 1.2 Å/mm at 100 Å.

Hilger & Watts manufactures a three-meter-grazing incidence spectrograph and Jarrell-Ash Company a one-meter spectrograph (Fig. 23), a two-meter scanning spectrometer.

REFERENCES

1. ROWLAND, H. A., *Phil. Mag.*, **13**, 469 (1882).
2. EBERT, H., *Wied. Ann.*, **38**, 489 (1889).
3. FASTIE, W. G., *J. Opt. Soc. Am.*, **42**, 641 (1952).
4. CERNY, M. AND TURNER, A. F., *Z. Physik*, **61**, 792 (1930).
5. BASS, A. M. AND KESSLER, K. G., *J. Opt. Soc. Am.*, **49**, 1223 (1959).
6. ROWLAND, H. A., *Phil. Mag.*, **16**, 197 and 210 (1883).
7. RUNGE, C. R. AND PASCHEN, F., *Abhand. d. K. Akad. d. Wiss. Z. Berlin*, Anhang 1 (1902).
8. ABNEY, W. DEW., *Phil. Trans.*, **177**, II, 457 (1886).
9. EAGLE, A., *Astrophys. J.*, **31**, 120 (1910).
10. SAWYER, R. A., "Experimental Spectroscopy," pgs. 154 and 290, Prentice Hall, N. Y., 1944.
11. SEYA, M., *Science of Light*, **2**, 8 (1952) Tokyo.
12. HOAG, J. B., *Astrophys. J.*, **66**, 225 (1927).
13. EDLÉN, *Nova Acta Reg. Soc. Sci. Ups.* **IV**, **9**, 6 (1934).
14. TYRÉN, F., *Z. Physik*, **111**, 314 (1938).
15. WADSWORTH, F. L. O., *Astrophys. J.*, **3**, 54 (1896).

R. F. JARRELL

HISTORY AND ORIGIN

History of Optics to about 1600

Time and again archaeological discoveries are reported which allegedly show that the ancients knew about the use of optical lenses for improving the recognition of small objects and possibly for assisting malfunctioning eyes. Examples are: (1) the discovery of convex quartz lenses of 1 to 3 inches in diameter and a refractive power of 5 to 8 dioptries on Crete in the Mediterranean Sea in 1930; (2) the discovery of glass lenses of about $1\frac{1}{2}$ inch in diameter and $5\frac{1}{2}$ dioptries in a stone coffin found at Carthage (Africa) in 1914.

These lenses demonstrate remarkable technical skill and, so some historians assert, their optical magnifying power is so obvious that it could not escape detection. Hence, practical use of simple optical instruments in times of antiquity seems highly probable. The counterarguments emphasize the scarcity of these findings and the complete lack of reports about applications and also about trade activities which certainly would have served a wider distribution of optical instruments with their wonderful properties.

In reconciliation of these opinions it can be safely assumed that there were instances in ancient times when a lonely tinkerer might have treasured a ground and polished gemstone and made what might be called playful experiments. We do not know about them. They remained without consequence in the future. These early experiments can be considered to be forerunners of later discoveries but they certainly were not the first steps of the development of an art. In the same sense Archimedes cannot be called the founder of hydromechanics; nor should Seneca be given credit for having established the foundation of spectroscopy because he observed the appearance of colors in looking through a triple-faced piece of glass.

The possibility of the use of lenses as burning glasses for concentrating the heat

of the sun must also have been an early observation. It was first mentioned by Aristophanes about 423 B.C.

The process of seeing and perceiving objects, shapes and colors attracted many philosophers of antiquity. An explanation of these phenomena was found in the assumption of visual rays emanating from the eyes by Plato about 400 B.C. in his *Timaeus*.

Empedocles of Agrigent, about 450 B.C., had assumed two different kinds of visual rays, one coming from the eye and the other from the body observed. The latter penetrates through pores into the sense organ and an image is formed from the interaction of both.

Democritus of Abdera, a contemporary of Plato, did not accept two kinds of visual rays, but only one. He assumed that small particles are emitted by bright objects and hit the eye. This apparently quite modern concept is confused, however, by the notion that perception itself was explained by assuming the images, carried by the visual rays, mingled with the surrounding air and were then able to penetrate through pores into the eye where they reach the soul.

Aristotle, about 350 B.C., followed Democritus in opposing the assumption of visual ray emanations from the eye but went further in an attempt to explain color perception. Colors are brought about, he stated, by the mixture of light with darkness in the medium between the object and the eye. The thin medium of fog makes the light of the setting sun appear red and the heavier and thicker clouds bring out more colors as, for example, in the rainbow.

Euclid of Alexandria, about 300 B.C., wrote several books on mathematics and physics. In his *Optics* and especially in *Catoptrics* he treated mathematically the geometric relations of the real and apparent sizes of object and image for different distances from plane and spherical mirrors. He stated the equality of the angles formed by reflected light beams traveling from and to

object and image. Also, he considered convergence or divergence of light beams reflected on spherical mirrors and studied the position of the focal point for varying conditions. With the clear formulation of the law of reflection a firm foundation of optics had been laid. By Euclid's contributions all problems of optical reflection were reduced to pure geometry. Because of the emphasis put on mathematics Euclid did not pay too much attention to the direction of the light beams in view of their geometric reversibility. It is a point of minor importance that Euclid retained Plato's erroneous assumption of the emanation of visual rays from the eye, in spite of Aristotle.

Widespread is the legend about Archimedes, about 250 B.C., concerning his application of burning mirrors for the defense of Syracuse: the ships of a Roman fleet allegedly caught fire from reflected sunlight and sank. Archimedes was indeed a great scientist and inventor who designed many war machines and experimented with concave mirrors.

Hero of Alexandria, about 100 B.C., is best known for his mechanic, hydromechanic and pneumatic investigations. Interesting is his version of the law of reflection in terms of a minimum principle: If one point in front of a plane mirror is the optical image of another located on the same side of the mirror, then the sum of the distances of the two points from the point of reflection on the mirror is a minimum. In other words, the light takes the shortest possible path. Then the angle of incidence is equal to the angle of reflection.

Cleomedes, about 50 A.D., investigated optical refraction and used the perpendicular at the point of incidence as reference. He described an experiment demonstrating refraction which had been falsely attributed to Euclid. A ring is placed at the bottom of a jar. When the jar is looked into in such a way that the ring just disappears behind the upper rim then it can be made visible

again by filling the jar with water. Also, Cleomedes pointed out that it is because of refraction that the sun can still be seen at sunset above the horizon when actually it lies below the horizon.

Seneca, about 40 A.D., noticed and stated that the colors of the rainbow are the same as those seen through a three-cornered piece of glass with a sharp edge. The latter colors he declares as false and only the rainbow colors as genuine. He also observed and described the optical magnification of an apple seen through a round glass bottle filled with water. It is significant for him and his time that from his optical observations he formed the conclusion that nothing is more deceptive than the eye.

Quite different in nature was the work of Ptolemy, about 100 A.D., who made the first quantitative investigations of optical refraction phenomena. His *Opticorum Sermones Quinque* is not only a summary of everything that was known at his time, but also of his own ideas on the theory of seeing, on reflection by plane and curved mirrors, and on refraction. In the last area he measured the angles of incidence and refraction between either two of the media of air, glass, and water.

Table 1 shows his results for air and water compared with data obtained experimentally by Vitello, about 1280 A.D., and computed from Snell's law which was published in 1662 and upheld ever since.

Ptolemy's remarkably accurate results were relied on as standard authority for hundreds of years. Today, they are considered by some historians as the oldest extant example of a collection of coherent experimental data.

From the results of his research in refraction Ptolemy also tried to explain the apparent paths of the circumpolar stars which are not perfect circles but curves similar to circles, only slightly flattened. Ptolemy did not improve upon the assumption of visual rays emanating from the eye; he just reports

it. Obviously, considerations about the nature of these rays do not enter mathematical considerations of their paths.

During the following 400 years no remarkable progress in optics was made. In about 530 A.D., Anthemius, the architect of the famous Hagia Sophia in Constantinople, reported his investigations on curved mirrors. He stated that light beams coming from a point source are united again in a point by reflection only when the mirror is elliptical in shape. He did not believe the legend about sinking the Roman fleet by Archimedes.

The next progress worth mentioning was made by the Arabian scientist Alhazen who died 1038 A.D. He broke definitely with the old theory of visual rays as emanations from the eye. The light must come to the eye from the objects observed and must have a definite, but not an infinitely high speed, he stated. He also treated mathematically in more detail than ever before, plane, spherical, conical and cylindrical mirrors with reflections both inside and outside. The so-called Alhazen's problem appealed to the skill of many mathematicians for a long time. It can be stated as follows: Find on a curved mirror the point of reflection of a beam going from a point source to the eye with both in fixed positions in reference to the mirror. Alhazen could not yet state the law of refraction, but he found the larger the non-proportionality of the refraction angles the more different the two optical media were in their density. He also knew the magnifying power of hemispherical lenses which he felt must be put in immediate contact with the object.

Roger Bacon (1214–1294) can be called the first scientist, in the modern sense, of medieval times. In his works he still referred to Ptolemy and Alhazen but he widened the horizons in all directions. He used geometric construction of light paths on mirrors and found for spherical mirrors the focal length depending on the distance from the axis of symmetry. For parabolic mirrors he

was able to determine the exact position of the focal point and he gave suggestions about how to make such mirrors. It is uncertain, however, if he had made one himself. Bacon treated the magnifying power of plano-convex lenses but he still thought that they should be put on the object for observation. With great enthusiasm he described the optical magnification of distant objects and it is obvious that he had experimented with single lenses. However, there is no indication of the application of telescope-like arrangements, or of combinations of lenses. Most of his work was forgotten after his death and his influence on contemporary scientists and those of the following 200 years was negligible.

One of Roger Bacon's contemporaries, Vitello (1270) collected and rewrote the works of the older opticians and added a few of his own observations. He explicitly stated that the angles of refraction between two media stay constant when the direction of travel of the beam is reversed. Results of his measurements of refraction are shown in Table 1. In his explanation of the rainbow he claimed that it is caused by both reflection and refraction in raindrops.

It had been known a long time that lenses can be used to improve the visual power of the eye. But it was certainly another difficult step to the development of spectacles for which a pair of suitable lenses had to be mounted together in rims with brackets in such a way that they could be carried in front of the eyes at the proper distance. Who was the first to suggest and make eyeglasses is not exactly known. In 1285 *Dizionario dell'Accademia della Crusca* named as inventor a Salvino degli Armati on whose tombstone in Florence was written "Inventore degli Occhiali" in 1317.

At about the same time (1310) Theodoricus described accurately the path of a light beam within a raindrop for the explanation of the rainbow, going further than Vitello. First, there is a refraction near the top of a

drop, then a reflection on the back, and finally another refraction near the bottom, when the beam leaves the drop; this brings about the main rainbow. The secondary rainbow is produced respectively by two-fold refractions and reflections. This lengthens the path of the light beam within the drop so that the exit angle is changed in such a way that the primary and secondary rainbows appear separate. In ignorance of the law of refraction, which was found about 300 years after his time, Theodoricus could give only scholastic philosophical reasons for the preference of nature for that complicated light path, and there were many scientists at his time and later who disagreed with him in this matter.

One of them was Maurolycus, about 1575, who taught mathematics and physics in Constantinople. He had recognized the function of the eye lens and could explain the effect of eyeglasses as means of optically compensating for the malfunctions of the eye lens.

Giambattista della Porta was a collector of *Miracula rerum naturalium* which he published 1589 in the second much improved edition of his *Magia Naturalis* and in his *De Refractione* in 1593. He was more a hobbyist than a scientist, it is true, but he certainly was a great experimenter who enriched many of his reports, which often appear almost foolish to us, with his own discoveries. So he improved the "camera

TABLE 1

Angle of incidence	Angle of Refraction (degrees)		
	Ptolemy	Vitello	Snell
10°	8	7½	7¼
20°	15½	15	15½
30°	22½	22	22½
40°	28	29	29
50°	35	35	35
60°	40½	40½	40½
70°	45	45	45½
80°	50	47½	50

obscura" which had been described by Leonardo da Vinci more than 50 years before him, by mounting a lens into the hole of the "dark chamber;" thus he obtained much clearer and brighter pictures. Also, he pointed out the similarity of the camera obscura to the human eye both in structure and in operation.

The camera obscura was further developed by della Porta. He put a tube in front of the lens with a thin paper screen at its end. There were small figures drawn on the screen which appeared highly magnified on the observation wall of the camera room when sunlight fell on the screen outside. Upon moving the tube or the figures on the screen the pictures on the wall would also move, much to the delight of the visitors of the inventor. They, of course, had to enter the chamber to make these observations. Since it did not occur to della Porta to make the whole arrangement smaller and portable, he cannot justly be called the inventor of the *laterna magica*, the forerunner of the modern optical projector. The usefulness of a portable optical projector seems so obvious that we cannot see how della Porta could have missed this invention.

Also, it is difficult to understand why the compound microscope was not invented earlier. The first report about the formation of guilds of spectacle makers came from Flanders in the first half of the 14th century. Certainly there were experiences in the shops of these opticians with combinations of two or three glass lenses. But from that time it took about 200 years until the effects of such combinations were fully recognized. The invention of the compound microscope is dated at about 1590 and of the telescope at 1608. Both instruments opened new worlds for everybody who cared to use them, but their appreciation depended decisively on the cultural background and on the readiness to look for those new worlds. With the telescope the expansion of the range of the human eye was much more obvious than

with the microscope. So it is no wonder that much more attention was given to the telescope than to the microscope in the seventeenth century.

Invention of Microscope and Telescope

Combinations of lenses are mentioned early, and the greater magnification obtained by a combination of lenses was often recognized. Examples are the writings of Fracastorius about 1550, and Cabaesus, about 1600, who mentioned such earlier reports. In these older reports it is sometimes not clear whether a microscope or a telescope is meant or even an instrument with fixed position of the optical parts.

However, it seems to be certain that the telescope was invented about 1608 in Holland because this year is mentioned several times by the first authors writing about this instrument.

In order to get at the truth concerning early priority claims in a court investigation in Middelburg, Holland, 1654, it was established by witnesses and documents that the manufacturer of spectacles Zacharias Jansen and his son Hans had made telescopes in Middelburg after 1590 and before 1609. They consisted in a combination of one convex and one concave lens and had a length of 15 to 16 inches. Allegedly, the glass grinder Lippershey had learned the art from them and produced telescopes for sale after 1609. Documents show that he had submitted a request that an "Octroi" be granted to him. This would be called a patent today. A government committee checked his claims and asked him to make two instruments to see with both eyes, obviously for military purposes. On February 13, 1609, he had these instruments made and delivered to the government. A prize was granted to him but an octroi was refused because others had knowledge about the design of telescopes.

News of this invention had reached Galileo Galilei in Italy in June 1609. Understand-

ing the optical principle involved he made a telescope himself and exhibited it in Venice "for more than a month, to the astonishment of the Heads of the Republic." He kept on improving his instrument until, in January 1610, he had one with a magnifying power of 30 times. It is this instrument with which he made his fundamental discoveries of the mountains of the moon, of the moons of Jupiter, and others.

Nowadays it is practically impossible to name a single inventor both for the telescope and for the microscope. On the one hand, Zacharias Jansen does not seem to have built a telescope at all, but a microscope, and we have the word of no less an authority than Christian Huygens for it. Also, Jansen appears today in a suspicious light because he had embezzled false Spanish money which he had coined on order of his government to ruin Spanish credit. He was condemned to death but escaped from prison.

On the other hand, telescopes had been on sale in France early in 1609. Also, at the Frankfurt Fair in Germany an itinerant Belgian had shown a telescope around in the fall of 1609. In Milan, Italy, "Dutch Trunks, Perspectives or Cylinders," as they were called, appeared, as well as in Venice, Padua, and London. In consideration of these facts the decision of the Dutch Government to refuse the grant of a patent to Lippershey seems to be justified.

Spectral Phenomena, 1600-1800

The first observation of spectral colors other than those in the rainbow is probably the one reported by Seneca who lived about 40 A.D. However, he claims that both phenomena are quite different in nature. Their similarity or even equality was first pointed out by Maurolycus in 1575 A.D. The same opinion was expressed by Descartes in 1637. About ten years later in 1648 M. Marci described in his book *Thaumantias* his observations of spectra in detail. He placed a prism in front of a hole in a dark room and

observed a spectrum which he called "iris trigonia." He noted that the colored rays diverge after leaving the prism and that they are refracted to a different degree. He also stated that the colored light when it passes through a hole in the screen does not change its color again when it hits a second prism. This is really the famous "experimentum crucis" performed by Newton and published twenty-four years later in his *Opticks*.

Grimaldi performed what could be the first experiment with diffraction gratings by making fine and regular scratches on a metal surface. In his book printed in 1665 he compared the diffraction spectra with those obtained with a prism.

The most comprehensive investigation of that time however was performed by Newton, who reported his results and conclusions in a letter to the Royal Society on February 6, 1672. His whole theory appeared in *Opticks* or a *Treatise of the Reflections, Inflections and Colours of Light* in 1704. There is another publication by Newton covering his lectures in 1728 which, however, does not go beyond the *Opticks*.

In Book One of the *Opticks* Newton describes how different-colored pieces of paper appear displaced and draws the conclusion that the colors are refracted to a different extent. Then he describes how a spectrum originates from white light when a light beam can penetrate through a hole into a dark room and a prism is placed in its path. Newton recognized the spectrum as a superposition of infinitely many images of the hole, each in its own special color. He observed that the spectrum is purer when a rectangle is used instead of a hole, and he recommended narrow slits for the extreme case of exceptional purity of colors which, however, are not very bright in this case. Newton proved that the colored light beams are really not produced by the prisms by using many different substances for them with which he obtained the same results. He also

showed that light of a special color has its own characteristic refrangeability.

In Book Two and Book Three (interference and refraction phenomena) the rainbow and the color of physical objects are treated.

The most important result of Newton's *Opticks* can be stated as the demonstration that it is not the white light which is simple or fundamental, but that it originates from the combination of all the other possible colors. A certain color is defined by its refrangeability and its refraction coefficient for a certain prism material. There are infinitely many colors with homogeneous transitions from one to the other; for practical purposes, however, Newton distinguished seven main colors.

It is remarkable that Newton in spite of his very diversified and detailed investigations did not find the Fraunhofer lines but the explanation can probably be found in the inferior quality of his prisms which were full of spots and striations; also the quality of polishing was certainly not too good at that time.

The authority of Newton remained unchallenged for a long time, with the consequence that some of his errors were uncorrected. One example is Newton's erroneous assumption of the strict proportionality of refraction and dispersion which leads to the impossibility of making achromatic lenses. In these, the refraction is used for the formation of the optical image and the chromatic dispersion is suppressed as much as possible. Newton's authority had been used time and again in later years to prove that such lenses could not be made.

In 1747, Euler had assumed that the dispersion depended on the refractive index, and developed a mathematical relation based on this assumption. Although he later abandoned this idea, it suggested the possibility of making achromatic lenses to Dollond who succeeded in making the first achromatic objectives in 1758 "after numerous trials and a resolute perseverance." Certainly, Dollond

had worked hard on his optical experiments, but it is also true that he had had a wide correspondence with the opticians of his time, as with Euler, and Klingenstjerna, and that he had obtained information about the work of Ch. M. Hall who had been his predecessor in 1729. Nowhere, however, does Dollond express his recognition of the work of these men; he does not even mention their names.

Observation of Lines Within and Without the Spectrum, 1800–1860

An important progress in the theory of dispersion was made by the discovery of the Fraunhofer lines which permitted for the first time the measurement of the refrangeability of the rays at definite locations in the spectrum. These lines had been seen first by Wollaston in 1802, when in a dark room he had looked through a prism directly at a narrow slit in the window screen. He describes the spectrum of the sunlight to be not continuous, as had been generally assumed at that time, but divided into several distinct colors by sharp and dark lines. He states that these lines can best be seen if the prism is held in such a position that the light beam suffers a minimum of refraction. There can be no doubt that Wollaston had actually seen the Fraunhofer lines but nothing came of his discovery, and it has been completely forgotten for a long time.

Eleven years later, Fraunhofer, an optician and instrument maker, rediscovered the dark lines in the sun spectrum and knew how to make the best use of this observation. He reported his discoveries, first in lectures, in 1814 and 1815, and later, in 1817, in a publication. In this and his later publications Fraunhofer did not try to establish any theory about the origin of the bright or dark lines in the spectrum; however, the progress made by him is very important. It can be summarized in the following way: First, the spectrum of the sunlight has dark lines at certain invariant positions which permit the

designation of accurately determined wavelengths for these and other positions in the spectrum. Secondly, it was found also that the other celestial bodies have lines in their spectra which, however, can be different from those of the sun spectrum. Thirdly, it was found that apparently all light sources on the earth have dark or bright lines in the spectrum.

In 1821 Fraunhofer investigated the influence of one or several slots on a light beam passing through them and as a result of his investigations he invented the diffraction grating. He made a great number of these new devices and used them for the first determination of the wavelength of the dark lines in the spectrum which were called Fraunhofer lines after him.

Two years later, in 1823, J. F. Herschel published the first crude pictures of emission spectra as plots of intensity versus spectral color. He investigated burning sulfur and alcohol in which was dissolved a salt of strontium, barium, mercury, copper, and boron. He found that also many other salts color the alcohol flame both as solutions and as powders put on the wick. Herschel wrote in 1831: "The colors thus communicated by the different bases to flame afford in many cases, a ready and neat way of detecting extremely minute quantities of them." No doubt, Herschel had thought about spectral analysis but did not bring this idea to fruition. Also, he described how a flame with very bright yellow light can be produced when certain materials, as for example, sulfur, are thrown into a very hot crucible and that in such a case almost no other colors are detectable. So, he thought that the light of the same color can come from different materials and that the spectral colors depend on the temperature of the flames. The reason for this false opinion was the ubiquitous presence of sodium, the bright yellow line of which would subsequently deceive many other investigators.

In 1833, and in later years, Sir David

Brewster published his results of investigations of absorption spectra of colored substances. He thought that the variety of the bands observed is brought about by a superposition of single bands each of which would belong to one single element. He studied vapors of sulfur, arsenic, and iodine. Nitrous acid vapor showed a spectrum which did not fit his ideas at all. It consisted of a large number of short, fine black lines which Brewster could not understand; he counted more than 2,000 of them. He compared this spectrum with the one given by sunlight and believed that he had found many coincidences. For these studies he prepared a new drawing of the sun spectrum which was twelve times as long as Fraunhofer's map. The deviations from Fraunhofer's original drawing Brewster explained by the assumption that the sunlight had changed since Fraunhofer's studies.

Brewster found also that the sun spectrum varies with the time of the day and with the season. He drew the conclusion, in 1832, that certain lines are brought about by the earth atmosphere and he called them "telluric lines." The other lines which did not change he ascribed to the sun where they are brought about by absorption in the sun's atmosphere.

In 1831 Brewster had published and defended for 25 years a strange deduction from experimental investigations concerning spectral colors. He thought that they are not pure but that everyone of them contains also all the other colors of the spectrum. A part of them would always combine into white light and the remainder would determine the apparent color. A definite color cannot be associated with a definite refractive coefficient and vice versa. In spite of serious criticism by other contemporary scientists Brewster tenaciously clung to his ideas. Helmholtz published experiments in 1852 which demonstrate that Brewster's results can be understood by diffused white light present in all parts of the spectrum. However, Brewster did not give up his wrong

ideas and brought forth new, but not very convincing, arguments even in his last publication in 1866.

In the meantime many new observations on spectra had been made, for example by Miller who reported in 1833 his studies of lines and bands in the absorption spectra of bromine, iodine, and chlorine.

In 1826, also W. H. Talbot had come close to the discovery of spectral analysis in stating "... a glance at the prismatic spectrum of a flame may show it to contain substances which it would otherwise require a laborious chemical analysis to detect." However, Talbot does not come to any further conclusions and it is not possible to ascertain how he arrived at his idea. He described detailed experiments and reported the results but strangely enough they were not taken by him as proof. To the contrary, he wrote that one and the same yellow light had been emitted by burning sulfur, a burning mixture of kitchen salt, soda, and sulfur, diluted alcohol, or a platinum sheet touched with a finger or with a piece of soap. He stated that he is especially puzzled by the optical analogy in the behavior of sulfur and soda, "which do not have anything in common."

Later publications by Talbot, in 1834 and 1835, are much clearer and constitute real progress. He described the flame spectra of strontium and lithium and stated "... I hesitate not to say that optical analysis can distinguish the minutest portions of these two substances from each other with as much certainty, if not more, than any other known method." Investigations, published by Talbot in 1871, on torch flame spectra of calcia are less clear in results and interpretations. He also described spark spectra of several metals, which he "burned electrically." In connection with these experiments he said: "the yellow rays of the salts of soda possess a fixed and invariable character."

A step forward in the right direction was made by C. H. Wheatstone whose investiga-

tions were published first in an abstract in 1835 and as a detailed report much later, in 1861, which was after the publications by Kirchhoff and Bunsen. Wheatstone observed spark spectra of mercury and molten metals by means of a prism and a telescope. The position of the lines could be measured with a micrometer scale in the eyepiece. He found the lines very sharp, bright and different for each metal. He stated: "these differences are so obvious that any one metal may instantly be distinguished from the others by the appearance of its spark and we have here a mode of discriminating metallic bodies more ready even than a chemical examination, and which may be hereafter employed for useful purposes." Wheatstone also developed ideas about the mechanism of light emission and thought that "the peculiar luminous effects produced by electrical action on different metals depend, no doubt, on their molecular structures; and we have hence a new optical means of examining the internal mechanism of matter."

During the three decades before Kirchhoff and Bunsen many investigations and theoretical considerations were devoted to the "true" nature of the spectra observed. Often it was not clear whether a certain spectrum came about by emission or absorption alone or by a superposition of both. So, in the description of the emission spectrum of copper Talbot said that salts of copper emit spectra which are so covered by dark lines that they appear similar to the sunlight spectrum. In the description of emission spectra many authors of that time indicated where they found dark regions in the spectrum, thinking that these were the characteristic features and not the bright lines between them.

Herschel had been widely criticized for his alleged discovery of heat radiation outside of the visible spectrum on its red end among others by Leslie in 1802, Prévost in 1802, Böckman in 1811 and Meikee in 1825. Other investigators particularly Englefield in 1802

and Ritter in 1803, confirmed, more or less, Herschel's findings. Some experimenters had varied the materials of which their prisms were made and, depending on the kind of material, they found the maximum heat effect either beyond the visible end, confirming Herschel, or within the visible spectrum. Among these were Wünsch in 1807, Bérard in 1817, and especially Seebeck in 1818. The reasons for these wide disagreements were doubtless imperfections in the experimental means. Nowhere had "pure" spectra been observed because no slits had been used yet. The spectra studied were mostly just elongated images of the sun with one red and one violet end. It is significant that several investigators of that time even talked about the "white" region of the spectrum. The natures of heat and light were not yet understood, and by many they were thought to be special kinds of matter. Also, no difference had been recognized between conducted and radiated heat.

It was mentioned before that all scientists active in optical research at that time, had been seriously misled in their investigations by the ubiquitous presence of sodium because the yellow sodium line which is so bright in its appearance was naturally found in many other spectra. So Herschel was of the opinion that one and the same light can be emitted from different substances and the kind of the emitted light does depend only on temperature. He was able to show that some substances give a characteristic spectrum but not that one spectrum is characteristic for a certain substance.

The confusion had been increased by the discussions following the discovery of chemical effects in the spectrum at its violet end and in the adjoining invisible region by Ritter in 1801.

So, in 1832, Brewster stated and maintained for a long time that there were not less than five distinctly different kinds of optical light: Three visible colors and on one end of the spectrum the heat rays and on the other

the chemical rays. But all five are simultaneously present in all parts of the spectrum in mutual superposition.

However, this period of uncertainty and endless argumentation came to an end around 1860 with the investigations of Kirchhoff and Bunsen.

Development of Spectral Analysis

Bunsen and Kirchhoff published the results of their first investigations in 1859. They had introduced ordinary kitchen salt into flames of different temperatures and admitted sunlight through the flames into the slit of a spectroscope. They found that they could strengthen, weaken and even reverse the dark D-lines of the spectrum. Kirchhoff drew the conclusion that the dark lines in the sunlight spectrum come about because in the atmosphere of the sun are those materials present which produce in a flame bright lines at the same positions. Because the D-lines are dark with a salt flame of lower temperature, he concluded that the hot body of the sun is surrounded by a gas atmosphere of lower temperature and that sodium exists in the atmosphere of the sun as is indicated by the D-lines. For more detailed studies Kirchhoff had made a drawing of the solar spectrum which was eight feet long.

The most meticulous work in this field was done by Ångström, who published the positions of about 1200 lines of the solar spectrum in 1868; 800 of his lines could be identified as lines of elements known on the earth. As a unit he used the ten-millionth part of a millimeter which is named an angstrom unit after him.

Ångström had used a reflection grating for his measurements instead of a prism because it has certain advantages. For instance, the regular reflection which a grating produces is very nearly proportional to the wavelength. Hence, the wavelengths and the distances between the lines can be measured on a uniform scale.

The first gratings, for example the one used by Ångström, were not very fine. They might have had about 5000 lines to the inch. The art of making good gratings was later developed to an unprecedented perfection by H. Rowland, professor of physics at Johns Hopkins University, who spent many years in perfecting automatic ruling machines for the production of fine optical gratings. Some of them have more than 14,000 lines to the inch and a length of about 6 inches. Replicas of these gratings are still made. Rowland's tables of solar spectrum wavelengths contain about 20,000 lines and were considered standards up to recent times.

Kirchhoff had generalized his results and conclusions in the statement that for all wavelength and all physical bodies the emissivity is proportional to the absorption, both taken at the same temperature. The ratio of these two quantities depends only on the wavelength and the temperature and is equal to the emissivity of the absolute black body.

The practical application of their optical principles led Kirchhoff and Bunsen to the discovery of rubidium and cesium in 1861. With the same methods, thallium was discovered by Crookes in 1862 and indium by Reich and Richter a little later.

During the years after the first publications by Kirchhoff and Bunsen a violent discussion started concerning the priority of their discoveries. Nowadays, there seems to be complete agreement among the historians that claims of an earlier priority, stated either by or in behalf of men like Ångström, Thomson, Stokes, Stieren, Alter, Talbot, Steward, and others, are not justified. It must be admitted that many of these earlier investigators came close to the foundations of spectroscopy but they did not find the bricks still to be laid in order to erect the proud edifice of spectral analysis. Not one of them recognized the fundamental relation between emission and absorption which was going to lead to the success which Kirchhoff and Bunsen had. A few examples were men-

tioned in the foregoing text. If a reader would be interested in details of these arguments, he is referred to the many pages which Kayser wrote about this subject in his handbook (see references).

In technical respects, an important application of spectral analysis was Fraunhofer's early investigation of the spectra of celestial bodies. In order to give the stars' spectra sufficient width he had used a cylindrical lens. Such a lens was also used by Huggins in his famous investigations of 1863. On the same day when his paper was read to the Royal Society, news arrived in London that L. M. Rutherford in the United States had made similar observations. Later it was found that at about the same time Secchi in Rome and Vogel in Potsdam had also entered the field of stellar spectroscopy. It is not strange that under these circumstances there followed a redundancy of publications in this field. Only a few cases can be mentioned here which seem to be remarkable in certain respects.

In 1864, Huggins discovered the gaseous nature of the "unresolved" nebulae which had so stubbornly resisted the optical resolution into single stars by even the largest telescopes.

In 1868, Janssen turned a high-dispersion spectroscope tangentially to the sun and saw the shape of hydrogen prominences in the light of a hydrogen line. Lockyer had had the same idea and had ordered a special instrument for the observation of the phenomenon in the same year. Much to his dismay the delivery had been delayed, but both scientists agreed to share the honor of priority. The importance of their discovery lies in the fact that it now became possible to see the prominences at any time, not only when an eclipse occurred, if only a suitable spectroscope was available. Its high dispersion would weaken very much the diffuse light from the sun body, whereas the monochromatic light would not be affected.

This experience showed the importance of

the construction of spectroscopes with higher and higher dispersion which is made possible by the use of more and more prisms with the necessary precise mechanisms for moving them in a controlled way. This development to ever higher optical and mechanical perfection is still going on at the present time. Also, today only few observations are still made with the eye directly, and the photographic plate is widely used.

It is the combination of the photographic plate with a movable spectroscope slit which is the basic idea of the spectroheliograph. In this instrument an image of the sun is thrown on the slit plane of a spectroscope and moved across it so that all parts of the sun and its atmosphere can throw light through the slit. This light is then dispersed by one or several prisms and a narrow region of the spectrum is isolated by another slit which is fixed and permits only light of a certain wave length to pass. This light strikes a photographic plate upon which an image of the sun is formed in the light of a particular wavelength because the plate is moved simultaneously with the entrance image of the sun. This is a simplified explanation of the principles involved which found several modifications in later years. The most important contribution to this field came from G. E. Hale who developed his instrument between 1891 and 1895. With later instruments of higher perfection Hale attained, in 1908, pictures of the sun in the light of one of the hydrogen lines which showed that the sunspots had a vortex-like structure which made it possible to understand the formation of strong magnetic fields from the movement of charged particles (ions).

A difficult problem of solar research is presented by, what is called, the corona, the outermost parts of the sun atmosphere. Its light is so faint that all instruments, including the spectroheliograph, failed in recording it. Great success was achieved by B. Lyot of the Mendou Astrophysical Observatory who had the solar image formed on a black disc

which absorbed the direct glaring light. Then, by an ingenious arrangement of lenses behind this disc of his "coronagraph" he had enough light left to illuminate a spectrograph and obtained the first complete spectrum of the sun's corona in 1931 without an eclipse.

The reader of more general interests to whom this instrumentation of modern astrophysical research, the main instrument of which is still the spectroscope, seems too intricate or involved must be warned not to enter a modern industrial spectro-analytical laboratory. There he will see instruments which are still called "spectroscopes" or possibly "spectral analyzers" but they are actually complicated automatic machines with which a sample containing a dozen or more components may be analyzed in a few minutes consecutively or simultaneously. No attempt is made in this historical section to deal with these products of modern spectroscopical development. Examples are given in other parts of this encyclopedia.

REFERENCES

- "A History of Science" by G. Sarton, Harvard University Press, Cambridge, Mass. 1. vol. 1952. 2. vol. 1959.
 - "Ancient and Medieval Science in the Renaissance" by G. Sarton, University of Pennsylvania Press, Philadelphia, 1955.
 - "Moments of Discovery," Basic Books Inc., 2 vols., New York, 1958.
 - "A Source Book in Physics" by W. F. Magie, McGraw-Hill, New York, 1935.
 - "The History of the Telescope" by H. C. King, Sky Publishing Corporation, Cambridge, Mass., 1955.
 - "Handbuch der Spectroscopie" by H. Kayser, S. Hirzel, Leipzig, 1900.
 - "Geschichte der Physik" by E. Hoppe. F. Vieweg, Braunschweig, 1926.
 - "Die Geschichte der Physik" by F. Rosenberg. F. Vieweg, Braunschweig. vol. 1-3, 1887-1890.
 - "Die Naturwissenschaften in ihrer Entwicklung und in ihrem Zusammenhang" Leipzig, W. Engelmann, Vol. 1-4, 1920-1923.
- Also numerous articles in *Isis*, *American Scientist*, *Science*, and others.

E. K. WEISE

HOLLOW CATHODE DISCHARGE TUBES,
ANALYTICAL APPLICATIONS

The hollow cathode source, originated by Paschen⁹ and developed largely by Schuler,¹⁰ has been extensively used for the physical analysis of spectra.¹¹ In the past fifteen years there has been increased interest in the use of the hollow cathode source in chemical analysis. This is a logical development since this source as compared to the arc and spark sources in air has greater stability, greater reproducibility, and longer lengths of excitation with little increase in background.

The discharge tube consists of an anode and a cylindrical, hollow cathode enclosed in a vacuum tight chamber. The chamber has a quartz window so that the discharge in the tube may be observed, an inlet and outlet so that a rare gas may be circulated, electrical connections for the two electrodes, and water jackets for cooling the electrodes. The tube may be operated with any stable dc power supply capable of giving at least 1.00 amp at a few hundred volts.

Cooling the electrodes is required to keep the line breadth to a minimum. For extremely narrow lines liquid air cooling may be employed.²

The rare gas used in the discharge may be cleaned by one of two methods. The most efficient cleaning is accomplished by circulation of the rare gas through an all glass apparatus containing, among other things, a high ac voltage magnesium electrode discharge, a heated CuO trap, and several liquid-air cooled traps.³ The second method⁴ utilizes an activated uranium getter and is much simpler but less efficient.

The excitation mechanism of the hollow cathode differs quite radically from that of an arc or spark discharge. After the tube has been outgassed and rare gas has been admitted, the discharge is started by applying a potential of about 1,000 volts. Upon application of this potential free electrons are accelerated toward the anode through a

high potential field where enough kinetic energy is picked up to ionize the rare gas atoms by collision. Secondary electrons thus formed are accelerated toward the anode, while the newly formed ions accelerate toward the cathode.

The rare gas ions formed by this discharge are accelerated toward the cathode and upon collision with the sample in the cathode cavity sputter the sample into the discharge zone. The highly energetic rare gas ions then excite the sample atoms to emission through collision. Greater amounts of sputtering may be accomplished with the use of the heavier rare gases while greater excitation potentials may be obtained with the lighter rare gases.

Applications in Analysis. This tube has long been used in the physical analysis of spectra. Crosswhite, Dieke, and Segalreuer⁵ describe a hollow cathode source for use in the establishment of wavelengths and intensity standards. They investigated the effect of rare gas pressure, current, and type of rare gas used in the discharge. They found that with a regulated power supply and a sealed tube no fluctuations in intensities could be observed over a period of several days of continuous discharge. Other examples of physical analysis are listed in a bibliography compiled by the Jarrell-Ash Company.⁷

To date the hollow cathode has not been used extensively in chemical analysis. Its applications have mostly been limited to the analysis of the relative amounts of isotopes in natural and synthetic mixtures of elements and their salts. Brody, Fred, and Tomkins⁴ determined the relative amounts of L_1^7 and L_1^6 in natural lithium salts. Using the two isotopic lines close to 6707Å, they found the ratio L_1^7/L_1^6 to be 13.5 ± 0.2 .

In 1947 McNally, Harrison, and Rowe⁸ reported the successful determination of halogens and sulfur using the hollow cathode source. They state that 1 ppm fluorine could be detected in a 40-mg sample with exposures

of five minutes. A 20-mg metal oxide sample containing 30 ppm fluorine gave an average deviation of 15 %. Although no special emphasis was placed on the development of high sensitivity, one microgram of sulfur and 0.2 microgram of chlorine could be detected in 20-mg samples.

Adams and Burns at Westinghouse Corp.¹ are investigating the utilization of the hollow cathode tube in analysis of high purity iron, silver, germanium and silicon. They find that the density of lines occurring from copper impurities in high purity steel varies only 1 % in a series of constant time exposures. Also, they are able to determine 5 ppm chromium with as little variation and stated that with longer exposure times the sensitivity could be increased ten times.

Birks⁸ examined the effect of the current and the helium pressure on the line densities of the alkali metals and the halogens. With an order of precision of $\pm 10\%$, 0.1 μg F, 1 μg Cl, 5 μg Br, and 2.5 μg I could be determined. In a xenon atmosphere 0.01 μg Li, 0.05 μg Na, 0.05 μg K, 0.2 μg Rb, and 0.3 μg Cs could be determined. Birks also stated that it should be possible to obtain lower limits of detection since the lower limits of detection depend upon the time of exposure.

Although much investigation is yet needed, the hollow cathode tube appears to offer an excitation source for spectroscopy which has, in general, improved sensitivity, lower limits in the detection of trace elements, greater line resolution, and greater stability than the conventional arc and spark sources.

REFERENCES

1. ADAMS, K. B., BURNS, K., Westinghouse Co., Research Memo 6-94802-9-M37 (1957).
2. ARBORE, O. H., MACK, J. E., *J. Opt. Soc. Am.*, **40**, 386 (1950).
3. BIRKS, F. T., *Spectrochim. Acta*, **6**, 169 (1954).
4. BRODY, J. K., FRED, M., TOMKINS, F. S., *ibid.*, **6**, 333 (1954).
5. CROSSWHITE, H. M., DIEKE, G. H., SEGANGNEUR, C. S., *J. Opt. Soc. Am.*, **45**, 270 (1955).

6. DIEKE, G. H., CROSSWHITE, H. M., *ibid.*, **42**, 433 (1952).
7. Jarrell-Ash Co., 26 Farwell St., Newtonville 60, Mass. (March, 1958).
8. McNALLY, J. R., JR., HARRISON, G. R., ROWE, E., *J. Opt. Soc. Am.*, **37**, 93 (1947).
9. PASCHEN, F., *Ann. Physik*, **71**, 142 (1923).
10. SCHULER, H., *Z. Physik*, **72**, 423 (1931).
11. TOLANSKY, S., "High Resolution Spectroscopy," Methuen and Co., London, 1947.

DAVID R. RHODES

HYPERFINE STRUCTURE*

Under sufficient optical resolution spectral lines of many elements break up into a number of components. In most instances, the order of magnitude of these separations is much smaller than that of the fine-structure or multiplet separations that we have considered. Using the term somewhat loosely, hyperfine structure may be the manifestation of one of two distinct and physically unrelated effects or both may operate simultaneously. If an element consists of a mixture of isotopes, each will have its own set of energy levels, closely matching, but not identical. Accordingly each spectral line will be expected to have as many components as there are isotopic constituents, assuming that the relative abundance is sufficient in each instance for the appropriate transition to be observable. In present-day usage there is a commendable tendency to refer to this effect as isotope structure rather than hyperfine structure. In the instance of light atoms isotope structure arises almost entirely from the modification of the value of the Rydberg constant due to the variation in nuclear mass. This is in accordance with the previous discussion of hydrogenic ions and the isotopes of hydrogen. In the instance of heavy atoms, a number of other factors contribute, including a volume effect.

The operation of these other effects re-

* The seventh in a consecutively developed series of articles on the fundamentals of Optical Emission Spectra: see *Introduction: Designation and Description of Spectra* for list of topics, p. 202.

sults in different contributions to the various energy levels of the constituent isotopes with the consequence that patterns of different lines may differ significantly. Some of them may be sharp owing to the superposition of components. Study of isotope structure should lead to better insight into complex nuclear structure and possibly obtain evidence to support a choice between various suggested nuclear models.

True hyperfine structure results, according to presently accepted theory from the interaction of the total resultant angular momentum of the extranuclear electrons, represented by J with the angular momentum of the nucleus represented by I . This is a magnetic interaction in which both I and J precess about a resultant, F . This is strictly analogous to the treatment of the L - and S -vectors to form the resultant J in the instance of multiplet structure, and leads to analogous formulas for the interaction energy

$$\Gamma_F = A'IJ^* \cos(I*J^*)$$

which is equivalent to

$$\Gamma_F = \frac{1}{2}A'[F(F+1) - I(I+1) - J(J+1)]$$

where the quantum-mechanical expressions are understood to apply in the first instance. The second formula yields the same interval rule that applies to ordinary multiplets. The total width of a hyperfine pattern is proportional to the ratio of the nuclear magnetic moment to the nuclear angular momentum or mechanical moment. The latter quantity is readily determined from well-resolved patterns of classified lines, but the analysis of the splitting factors A' to arrive at the nuclear g factors is relatively difficult.

Deviations of hyperfine structures from the interval rule are accounted for on the basis of an assumed electric quadrupole moment, arising from a non-spherical distribution of protons in the nucleus. Values of these nuclear quadrupole moments have been determined for many atoms. A convenient listing of all known nuclear moments is to be

found in the latest "Key to the Periodic Chart of the Atoms."¹ These data were originally compiled by Klinkenberg.²

In general, hyperfine structures associated with nuclear moments are limited to nuclei of odd integral mass. This fact is taken into account in the selection of source elements for the establishment of wavelength standards of extreme homogeneity. A complete treatment of the subject of nuclear effects on radiation has been given by Kopferman.³

REFERENCES

1. W. F. MEGGERS, "Key to Periodic Chart of the Atoms," W. M. Welch Mfg. Co., Chicago (1959).
2. P. F. A. KLINKENBERG, *Rev. Mod. Phys.*, **24**, 63 (1952).
3. H. KOPFERMAN, "Kernmomente," 2nd ed., Akad. Verlagsgesellschaft, Frankfurt, A.M., (1956).

CURTIS J. HUMPHREYS

INTRODUCTION: DESIGNATION AND DESCRIPTION OF SPECTRA*

Optical emission spectroscopy is concerned with spectra originating in atoms or in ions of various stages. Essentially synonymous titles would be atomic spectra, or line spectra. This class of spectra is to be differentiated from those of molecular origin which are usually called band spectra. Spectra in that category are discussed in a separate article in this compilation entitled Band Spectra. In this discussion of emission spectra are also included line spectra that appear reversed or in absorption, of which the Fraunhofer spectrum of the sun and a preponderant majority of stellar spectra are conspicuous examples.

* The first in a consecutively developed series of articles by author on fundamentals of optical emission spectra, viz.: I. Introduction: Designation and Description of Spectra, p. 202; II. Precise Observation and Empirical Classification: History, p. 271; III. Bohr Theory: Introduction, p. 116; IV. Doublet Spectra, p. 148; V. Complex Spectra, p. 127; VI. Zeeman Effect, p. 328; VII. Hyperfine Structure, p. 201; VIII. Atomic Emission Spectra, Analysis of, p. 115; IX. Current Status of Emission Spectroscopy, p. 132; X. Applications, p. 112.

INTRODUCTION: DESIGNATION AND DESCRIPTION OF SPECTRA

Line emission spectra, which originate in gases excited to emit radiant energy, usually by electrical means, differ from the continuous spectra emitted by incandescent bodies, by exhibiting an array of lines characteristic of the source element and arranged in order of wavelength in accordance with the characteristics of the dispersing instrument or spectrograph. For practical purposes, these lines may be thought of as images of the slit of the spectrograph, each formed by light of a separate and distinct wavelength.

Probably the most distinctive characteristic of emission spectra is that each uniquely identifies its source element. No two spectra are alike. Of course, where a vast number of lines are involved, some fortuitous coincidences of lines occur. Most of these are resolved where sufficiently precise observation is possible. Because a spectrum provides an unchallenged signature or fingerprint of an element, the possibilities of spectroscopy for identification or analysis have been recognized from the beginning of the accumulation of detailed knowledge of the subject. Although present-day activity utilizing emission spectroscopy is mainly concerned with identification or chemical analysis, the development of currently accepted concepts of atom mechanics based on spectroscopic experimental material during the past half century constitutes an epoch-making achievement.

Since emission spectra are uniquely char-

was generally included in the designation. Thus, we had flame spectra, arc spectra, and spark spectra. Lockyer was the first to recognize that the increased complexity and different intensity distribution of the spectrum of a spark discharge, as distinguished from that of an arc, could be explained by the appearance of new lines of ionic origin, the intensification (enhancement) of others of the same origin and the suppression or weakening of atomic lines. Today we customarily specify the emitter in designating a spectrum. The designations, arc spectrum and spark spectrum are, however, sometimes used somewhat loosely, the first referring to an atomic spectrum, the second to one originating in an ion. The positive ions resulting from the removal of electrons are represented by the chemical symbol followed by one or more superscript plus signs, the number depending on the number of electrons removed. The use of a Roman numeral following the chemical symbol is customarily used to designate a spectrum rather than the ion. Thus, Fe I would be translated, the first spectrum of iron or the spectrum of atomic iron. However, a designation reading: The spectrum of Fe I, is regarded as tautological. The following tabulation is inserted to illustrate and clarify the modes of designation. The entries in each column are synonymous. Successive columns are used for spectra of successive stages of ionization.

Arc Spectrum of Iron	First Spark Spectrum of Iron	Second Spark Spectrum of Iron
First Spectrum of Iron	Second Spectrum of Iron	Third Spectrum of Iron
Fe I	Fe II	Fe III
Spectrum of Fe	Spectrum of Fe^+	Spectrum of Fe^{++}
Spectrum of neutral iron	Spectrum of singly ionized iron	Spectrum of doubly ionized iron

acteristic of the atoms of an element or of the atoms ionized to various stages, the name or symbol of the element is always included in any designation of a spectrum. In an earlier period of experimentation, since the character of a spectrum differed according to the mode of excitation, this information

The tabulation of experimental data obtained from the observation of a spectrum is generally called a description. Customarily such a description includes at least a list of wavelengths given in Angstrom units under the conditions of observation, the corresponding wave numbers which are the

reciprocals of the wavelengths expressed in cm^{-1} after correction to vacuum values, and a set of numbers indicating approximate intensities, which may be estimated or measured. An appropriate notation may be introduced to indicate peculiar properties of lines such as *wide*, *diffuse*, *unsymmetrical*, or *self-reversed*. The wavelength is usually observed and measured directly. The Angstrom unit for specifying wavelength is named for the Swedish scientist who introduced it, and is equal to 1×10^{-8} cm. The wave number which may be observed directly, but which is customarily derived from the wavelength, is expressed in reciprocal centimeters, conveniently written cm^{-1} . Some authors prefer to use the name *kayser* for cm^{-1} , but this usage has not been adopted officially. Published descriptions may also include the classifications or theoretical explanations of the lines.

Atomic emission spectra embrace a fairly broad interval of the electromagnetic spectrum extending from the soft X-ray region to the intermediate infrared. Lines have been observed with wavelengths as short as 6 Å, and at the opposite extreme, to give an example, as long as 125,000 Å, or 12.5 microns. Development of microwave techniques has provided a new method of observing some of the structural features of emission spectra. Radio astronomy, a new specialized branch of spectroscopy, makes use of essentially conventional radar methods. The interval comprising the region of visual perception, namely, 4000 to 8000 Å, and representing one octave of frequencies, is a relatively narrow region and only one of about ten octaves that contain essentially all observational data. Most of the interval in which emission spectra occur, including the extreme ultraviolet, is accessible to photography. The region of wavelengths beyond the photographic limit at about 13,000 Å is observable only by radiometric methods. It has received scanty attention, but owing to the invention of photoconductive detec-

tors, it is much more accessible than when first explored by Paschen half a century ago.

CURTIS J. HUMPHREYS

ION EXCHANGE-SPECTROSCOPIC PROCEDURES, TRACE ELEMENT ANALYSIS*

Introduction

The increasing interest in trace element impurities which may be present in many substances has placed added emphasis on methods for the detection and determination of extremely small quantities of material. Requirements for materials used in nuclear reactors, research in solid state, geochemical studies, and biological investigations, for example, often demand analysis for very low concentrations of impurity elements. Direct spectrographic examination has been applied extensively,¹ and perhaps all the classical methods of separation have been used to isolate or concentrate an element or group of elements prior to the analytical determination.^{2, 3} Utilization of ion exchange resins to increase the limits of detection is particularly attractive to the spectroscopist because quantitative separations can be made rapidly with simple equipment and the introduction of extraneous material to the sample minimized. Many of the published adsorption data obtained by radiochemical tracer experiments or other means have been readily adapted to performing separations before spectrochemical analysis. Applications of ion exchange techniques in the field of analytical chemistry are steadily increasing⁴ and have been reviewed periodically.⁵⁻⁸

Adsorbabilities have not been investigated thoroughly for the elements in all acids and particularly in mixtures of acids. Spectrographic analysis of column effluent solutions offers a rapid means of studying adsorption characteristics in a variety of solutes and determining optimum conditions of separation.

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

Analytical Applications

There are many materials which have the ability to remove ions from solution by an exchange process. Within recent years a variety of synthetic high capacity ion exchange resins have become commercially available⁹ and are being utilized for an ever increasing number of analytical operations. The properties of these ion exchange materials, the many diverse applications, and development of the theory is comprehensively described in several recent books,¹⁰⁻¹³ literature from various suppliers,¹⁴ and many other publications in this area. For the isolation of trace elements prior to spectrographic analysis strongly acidic cation exchangers containing sulfonic acid groups and strongly basic anion exchangers containing quaternary ammonium groups are especially suitable because of their high operating capacity and stability in strong mineral acids. Cation exchange resins are preferably used in the hydrogen form and anion exchange resins are converted to the required form by treatment with an excess of the solute to be used.

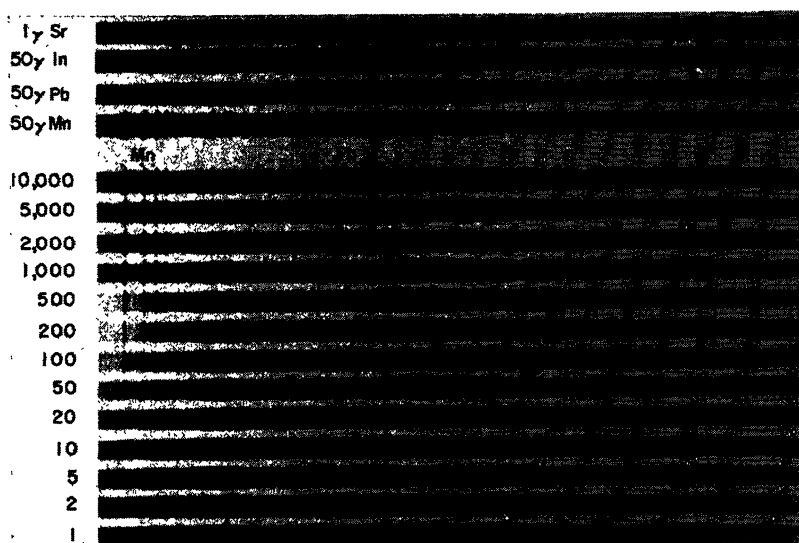
Employment of a resin column is usually preferred for analytical operations, although batchwise separations are sometimes convenient. The amount of resin in the column must exceed that necessary to adsorb the desired elements and may be estimated from the rated capacity or determined experimentally. In order to effectively use ion exchange resins, a solute is chosen in which the adsorbability of the impurity elements is markedly different than that of the matrix material. The degree of complexing can be controlled by varying the concentration of a chosen solute or introducing additional complexing agents. The most generally useful applications of ion exchange resins for spectrographic analysis are the single-pass separations in which the exchangeable ions are adsorbed on the resin bed and the non-exchangeable ions pass into effluent. Either the minor or the major components may be adsorbed. Whenever the impurity elements

are retained on the column they may be concentrated by ashing the resin or removed by a change of eluting agents. Judgment should be exercised when the resin is ignited, since some elements may be lost through volatilization. Adsorption of the sample matrix requires a somewhat larger resin column and subsequent concentration of impurities in the effluent by evaporation. In some instances the resin can be used indefinitely for similar samples by removing the adsorbed matrix ions and reconditioning the column.

Chromatographic separations, in which lesser difference of affinity for the resin is used to separate ions of like charge, have found a number of specific applications. A more rigid control of operating conditions is necessary to achieve reproducible elutions.

Spectrographic Features

Analytical determination of impurities can be made by an applicable spectrographic procedure. If the resin is ashed, the residue may be either analyzed by a direct excitation method or placed in solution. Determination of the impurities in the solution of ash or in the effluent solution can be performed by any of several spectrographic methods such as the porous cup,¹⁵ rotating disc,^{16, 17} graphite spark^{18, 19} or copper spark.²⁰ The procedures described below were developed using the copper spark method for analysis of column effluents. The high absolute sensitivity permits using small aliquots for the determination of a large number of elements, outweighing the disadvantage of not being able to produce results for Si and for some elements which are easily volatilized from hydrochloric acid solutions. Most results were obtained by visually comparing the sample spectra with previously prepared standard spectra (see Fig. 1) using a projection comparator. The resulting reproducibility of $\pm 50\%$ of the amount present was sufficiently accurate for trace element determinations and evaluation of a method. For



(Courtesy Argonne National Laboratory)

FIG. 1. Portion of a standard plate used for estimating Mn, Pb, In, and Sr (4025-4115 Å).

Milligrammas (10^{-9} g) of Mn, Pb, and In on the copper electrodes are given at the extreme left. For Sr the amounts are given near the line.

the determination of copper, graphite electrodes were used. The inadvertent introduction of foreign material is a very real problem in trace element analysis, requiring extreme cleanliness and the utmost precautions to avoid spurious results. Addition of such common elements as B, Na, K, Mg, Fe, and Al to the sample was kept at a minimum by using analytical grade or purified resin, high purity reagents, deionized water, and distilled acids. The columns, containers, and other equipment were made from polyethylene, quartz, or other easily cleaned or inert materials. Specific impurities introduced were identified and estimated by analysis of the effluent from a blank run.

The application of ion exchange techniques in conjunction with spectrographic analysis for trace elements is illustrated in the following brief summaries.

Determination of Impurities in Uranium and Plutonium²¹

A one gram sample was dissolved in hydrochloric acid and oxidized with the addi-

tion of a small amount of nitric acid. The U^{VI} or Pu^{VI} matrix was adsorbed on "Dowex" 1×10 , 200-400 mesh anion exchange resin from a solution greater than 6M hydrochloric acid using a polyethylene column containing about 10 grams of resin. The effluent containing the nonadsorbable ions was evaporated to a volume of 1 ml and the elements present estimated by the copper spark method. Impurities expected in this fraction can be predicted from the work of Kraus and Nelson²² and were determined to $\pm 50\%$ of the amount present by visual estimation. Limits of detection for the elements determined are given in the first column of Table 1. In the case of Pu, additional impurities such as Cd, Zn, Fe, Mo, and Ga were eluted by washing the column with 8M nitric acid, in which Pu^{VI} is still strongly adsorbed. After taking the effluent to dryness and redissolving in distilled hydrochloric acid, the solution was diluted to 1 ml and analyzed. The limits of detection for elements determined in this fraction are given in the second column of Table 1. This division of the sample into hydrochloric and

ION EXCHANGE-SPECTROSCOPIC PROCEDURES, TRACE ELEMENT ANALYSIS

TABLE 1. LIMITS OF DETECTION^a FOR ION EXCHANGE—COPPER SPARK METHOD (ppm)

Element	Impurities			Element	Impurities		
	In U and Pu(HCl)	Add'l. in Pu(HNO ₃)	In Th (HNO ₃)		In U and Pu(HCl)	Add'l. in Pu(HNO ₃)	In Th (HNO ₃)
Ag		2	2	Mn	0.05		0.05
Al	0.5 ^b		0.5 ^b	Mo		0.05	0.05
B	0.5		0.5	Na	1 ^b		1 ^b
Ba	0.1		0.1	Nd	0.3		0.3
Be	0.002		0.002	Ni	0.2		0.2
Ca	1 ^b		1 ^b	P	20		20
Cd		0.4	0.4	Pb	0.5		0.5
Ce	0.3		0.3	Pr	0.3		0.3
Co		0.2	0.2	Rb	0.3		0.3
Cr	0.2		0.2	Re		1	1
Cs	5		5	Rh		0.2	0.2
Cu	1		1	Ru		0.5	0.5
Dy	0.2		0.2	Sc	0.1		0.01
Er	0.1		0.1	Sm	0.5		0.5
Eu	0.02		0.02	Sr	0.002		0.002
Fe		1	1	Tb	1		1
Ga		0.1	0.1	Te		5	5
Gd	0.2		0.2	Th	0.5		
Hf	0.5		0.5	Ti	0.05		0.05
Ho	0.2		0.2	Tl		1	1
In		0.5	0.5	Tm	0.2		0.2
Ir		1	1	U		2	2
K	0.5 ^b		0.5 ^b	V	0.1		0.1
La	0.02		0.02	Y	0.005		0.005
Li	0.001		0.001	Yb	0.01		0.01
Lu	0.01		0.01	Zn		2	2
Mg	0.5 ^b		0.5 ^b	Zr	0.1		0.1

^a For a 0.1 ml aliquot of effluent from 1 g sample concentrated to 1 ml.

^b Limited by residual in blank.

nitric acid fractions reduces the possibility of matrix effects in the excitation of an impure sample.

Analysis of Thorium

A solution of a 1 g thorium sample in approximately 8*M* nitric acid was passed through a previously conditioned column containing 15–20 g “Dowex” 1 × 10, 200–400 mesh anion exchange resin. The thorium complex was adsorbed while a considerable number of elements passed through the column unaffected.²³ The effluent solution was evaporated to dryness, the residue dissolved in 1 ml distilled hydrochloric acid, and the impurities determined by the copper spark

method. Analysis for Sc, Y, and several of the rare earths was made to within ±5% of the amount present by a densitometric procedure²⁴ and estimations made of approximately 40 additional elements. The limits of detection for elements determined by the above procedure are given in the third column of Table 1.

In addition to the methods described, ion exchange has proved to be extremely convenient for application to analytical problems encountered in the laboratory from day to day. Traces of Cd were separated from aluminum by passing a 2*M* hydrochloric acid solution of the sample through an anion exchange resin column. The adsorbed Cd was

removed with dilute nitric acid and determined spectrographically. A similar procedure was used for determination of parts per million quantities of Zr in aluminum and to detect traces of U, Zr and Mo in cerium after separation in 12*M* hydrochloric acid. "Dowex-1" anion exchange resin was used to concentrate traces of Ta in uranium by a chromatographic elution in 20*M* hydrofluoric acid. Although removal of the uranium was not complete, 10 ppm of Ta could readily be detected in a 200 mg sample.

Several other useful applications of ion exchange for spectrographic analysis have been reported. In 1953 Welford, *et al.*²⁵ outlined a procedure for the isolation of trace quantities of Be from urine employing an anion exchange resin. The EDTA complex was adsorbed from a basic solution and determined spectrographically after elution with hydrochloric acid. Hettel and Fassel²⁶ employed a cation exchange resin to separate traces of rare earths from zirconium. The rare earths were adsorbed from a fluoride solution to which yttrium carrier had been added, removed from the column with hydrochloric acid, and determined individually using a direct current carbon arc method of excitation. A similar separation was used by Carter *et al.*²⁷ for the analysis of uranium in which rare earth elements were determined spectrographically after ashing the resin. Also, Hettel and Fassel²⁸ have reported a procedure for the determination of small amounts of rare earths in thorium after separation from a four molar hydrochloric acid solution using a cation exchange resin and have demonstrated the separation of this group from zirconium and uranium in a sulfate media. Ko^{29, 30} spectrographically determined Zr and several additional elements after separation from Pu by an anion exchange resin.

The Study of Elements Removed from Solution by Ion Exchange Resins

The anion adsorption of the elements from hydrochloric acid reported by Kraus and

Nelson²² is perhaps the most complete survey in this field and is extremely useful as a guide to performing separations prior to analysis. Adsorbabilities of elements from other media have not been thoroughly reported and their investigation can be lengthy, especially when facilities for radiochemical techniques of analysis are not readily available. Spectrographic analysis of the column effluent offers a relatively rapid means for determining the adsorption characteristics of some 60-odd elements in a variety of solutes. The principal advantage is the ability to determine, simultaneously, elution curves for a large group of elements. This technique has been utilized for the study of ions removed from hydrofluoric acid solutions by the anion exchange resin "Dowex-1".³¹ Adsorptions in a range of acid concentrations from 1 to 24 *M* were studied by using a series of eight columns to which microgram quantities of elements were equally added and subsequently eluted with a selected acid molarity. The effluents were collected in fractions which were analyzed by the copper spark method to determine the elution curve for each element at the selected acid concentration. Ions having no adsorption were readily evident. Distribution coefficients for those not strongly adsorbed were approximated from the location of the elution curve peak in ml using the expression $K_d = V/M$ presented by Tompkins^{32, 33} and Mayer,³⁴ where *V* = volume of effluent in ml and *M* = mass of resin. Element species which have a high affinity for the resin and require a prohibitive number of column volumes for their elution were indicated by "strong adsorption" or "greater than."

The above techniques have been employed together with chemical and radiochemical analyses in the study of elements adsorbed from nitrate media³⁵ by a strong base anion exchange resin. In all comparisons, the spectrochemically determined adsorptions were in excellent agreement with the results of both batchwise and column experiments

ION EXCHANGE-SPECTROSCOPIC PROCEDURES, TRACE ELEMENT ANALYSIS

TABLE 2. DISTRIBUTION COEFFICIENTS IN MIXTURES OF HCl AND 4M HF APPROXIMATED FROM SPECTROCHEMICAL ANALYSIS OF COLUMN EFFLUENTS

Element	HCl Molarity				
	0.2	1	3	6	9
Nb	160	36	37	138 ^a	95 ^a
Ta	>200	>200	>200	>200	95 ^a
Zr	119	11	<1.5	<1.5	<1.5
Hf	119	11	<1.5	<1.5	<1.5
W	155	17	6	2.5	5
Mo	75	16	7	16	102 ^a
Pd	>200	>200	154	46	21
Cd	166	>200	>200	79	17
Zn	12	>200	>200	89	41

^a Eluted in broad bands unsuitable for analytical separations.

where the other methods of analyses were employed. Similar agreement with adsorption data appearing in the literature for HCl-HF mixtures³⁶ was found in a spectrographic investigation³⁷ in which the effect of varying HF (1–8M) and HCl (0.2–9M) was studied for some 35 elements. The many possible separations apparent from the distribution coefficients presented in Table 2 for a group of elements simultaneously added to the columns illustrate the value of the described techniques in development of analytical procedures.

REFERENCES

1. "Symposium on Spectrochemical Analysis for Trace Elements" ASTM Special Technical Publication No. 221 (1957).
2. NORRIS, J. A., "Spectrographic Determination of Trace Elements in Metals," *ibid.*, P. 23.
3. NACHTRIEB, N. H., "Principles and Practices of Spectrochemistry," McGraw-Hill Book Co., Inc. New York, (1950).
4. "Symposium on Ion Exchange and Chromatography in Analytical Chemistry," ASTM Special Technical Publication No. 195, (1956).
5. KUNIN, R., *Anal. Chem.*, **32**, 67R (1960).
6. KUNIN, R., MCGARVEY, F. X., ZABIAN, D., *ibid.*, **30**, 681 (1958).
7. WALTON, H. F., *Ann. Rev. Phys. Chem.*, **10**, 123 (1959).
8. GREGOR, H. P. *ibid.*, **8**, 463 (1957).
9. Manufactured by The Dow Chemical Co., Midland, Michigan; The Permutit Co. Ltd., Gunnersbury Ave., London, England; Rohm and Haas, Philadelphia 5, Pa.
10. SALMON, J. E., HALE, D. K., "Ion Exchange—A Laboratory Manual," Butterworth's Scientific Publications, London, England (1959).
11. NACHOD, F. C., SCHUBERT, J. (Editors), "Ion Exchange Technology," Academic Press, New York, N. Y. (1956).
12. KUNIN, R., "Ion Exchange Resins," Second Edition, John Wiley and Sons, Inc., New York, N. Y. (1958).
13. JONES, A. G., "Analytical Chemistry Some New Techniques," Butterworth's Scientific Publications, London, England, P., 118–153 (1959).
14. "Dowex: Ion Exchange," The Dow Chemical Co., Midland, Mich. "Permutit Ion Exchange Resins in the Laboratory," The Permutit Co. Ltd., London, Eng.
15. Feldman, C., *Anal. Chem.*, **21**, 1041 (1949).
16. SVENITSKII, N. S., *J. Tech. Phys. (U.S.S.R.)*, **14**, 605 (1944).
17. PAGLIASSOTTI, J. P., PORSCHKE, F. W., *Anal. Chem.*, **23**, 198 (1951).
18. ZOTOV, G., FOWLER, C. A., AECL No. 298 (1955).
19. MORRIS, J. M., PINK, F. X., ASTM Special Tech. Pub. No. 221, P. 39 (1957).
20. FRED, M., NACHTRIEB, N. H., TOMKINS, F. S., *J. Opt. Soc. Am.*, **37**, 279 (1947).
21. BRODY, J. K., FARIS, J. P., BUCHANAN, R. F., *Anal. Chem.*, **30**, 1909 (1958).
22. KRAUS, K. A., NELSON, F., "Proceedings, International Conference on Peaceful Uses of Atomic Energy," **7**, 113, United Nations (1956).
23. BUCHANAN, R. F., FARIS, J. P., ORLANDINI, K. A., HUGHES, J. P., TID-7560 (1958).
24. FARIS, J. P., *Applied Spectroscopy*, **12**, 157 (1958).
25. WELFORD, G. A., PETERSON, G., FAST, J., HARLEY, J. H., *Anal. Chem.*, **25**, 517 (1953) (Abstract).
26. HETTEL, H. J., FASSEL, V. A., *Anal. Chem.*, **27**, 1311 (1955).
27. CARTER, J. A., DEAN, J. A., *Applied Spectroscopy*, **14**, 50 (1960).
28. HETTEL, H. J., FASSEL, V. A., A.E.C. Report ISC-851 (1956).
29. Ko, R., *Applied Spectroscopy*, **13**, 10 (1959).
30. Ko, R., A.E.C. Report HW-57873 (1958).
31. FARIS, J. P., *Anal. Chem.*, **32**, 520 (1960).

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32. TOMPKINS, E. R., *J. Chem. Ed.*, **26**, 32, 92 (1949).
33. TOMPKINS, E. R., MAYER, S. W., *J. Am. Chem. Soc.*, **69**, 2859 (1947).
34. MAYER, S. W., TOMPKINS, E. R., *ibid.*, p. 2866.
35. I.A.E.A. Conf. on Use of Radioisotopes in Physical Sciences and Industry, Copenhagen (1960).
36. NELSON, F., RUSH, R. M., KRAUS, K. A., *J. Am. Chem. Soc.*, **82**, 339 (1960).
37. FARIS, J. P. (unpublished results).

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ISOTOPE RATIO DETERMINATION, OPTICAL METHODS OF

The possibility of determining relative isotopic concentrations from optical spectra was realized as soon as observations of isotopic shifts in atomic spectra were made over twenty-five years ago. Several papers^{1, 2, 3} reporting isotope shifts included estimates of the relative concentration of the isotopes from intensity measurements which provided supporting evidence for the identification of the lines when compared with mass spectrographic results.

The optical method has grown in usefulness as an analytical tool in its own right due to several factors. First, the need for rapid, accurate isotope determinations has increased markedly during the past fifteen years due to the production and use of separated isotopes as a by-product of the atomic energy program, as well as the interest in the isotopic ratios of certain reactor structural materials and fuels.

The second factor is the improvement in the quality of optical gratings.^{4, 5} Since many of the shifts in atomic spectra are very small, large gratings which exhibit nearly theoretical resolving power are the most universally useful. Through improvements in the replication process, such gratings are now fairly common.

Still a third factor is the development and perfection of the scanning Fabry-Perot in-

terferometer by Jacquinot and his associates,^{6, 7, 8} and used by others,⁹ as well as improvements in the reflecting coatings by the use of multilayer films developed by Steudel¹⁰ and others.^{11, 12}

As the optical techniques have been refined, they have grown in interest, since they are capable of results independent of the mass spectrometer and in some cases are faster.

In principle, the method involves the relative intensity measurement of isotopic lines in much the same manner as conventional spectrographic methods. In the absence of self-absorption and with suitable instrumental conditions, the concentration of a given isotope is proportional to the peak intensity, and the relative isotopic concentration from the ratio of these intensities may be calculated.

Isotope shifts in atomic spectra are largest at the extremes of the atomic weight scale due predominantly to the mass effect in the light elements and the nuclear volume effect in the heavy elements. In progressing toward the middle of the weight scale, higher and higher resolving power is required to separate the isotope lines. Ultimately the shifts are too small to be resolved. However, shifts in molecular spectra where the isotope effect is strictly a mass effect are still observed and can be used for isotope assay.

Isotopic analyses have been accomplished by using mass spectrometrically analyzed mixtures of isotopes. A working curve is prepared in the conventional manner and carefully standardized conditions are maintained for standards and sample alike.

A more fundamental approach has been used resulting in isotopic assays completely independent of the mass spectrometer. In this case better resolution of the isotopic lines is required. Consequently conventional methods of excitation such as the d.c. arc or spark have been used only to a limited extent due to the Doppler, Stark, and other line broadening effects. However, uranium

isotope assays have been accomplished by sparking the metal directly.¹³ Hollow cathode tubes¹⁴ cooled with water or liquid air,^{15, 16} and electrodeless discharge tubes¹⁷ have proved more universally useful because of the sharp lines produced and the resulting improvement in the definition of close isotopic pairs or groups of lines. For example, the Li 6707A group excited in a water cooled hollow cathode tube and shown in Figure 1a, appears in the d. c. arc as a single broadened line.

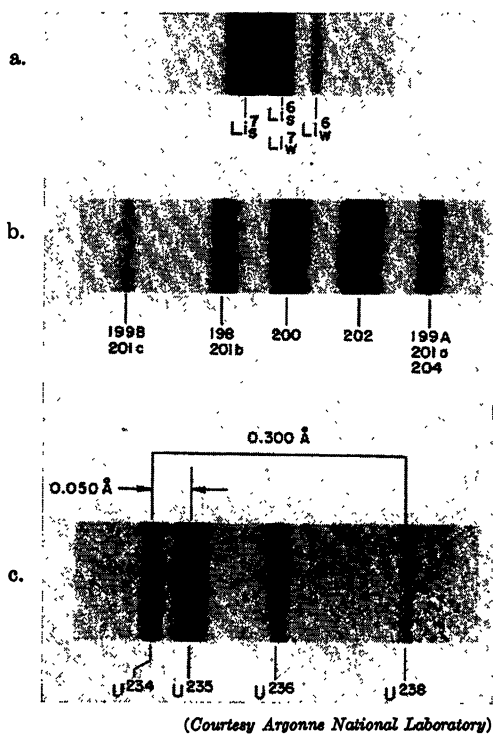
Saunderson¹⁸ using the former method has developed a rapid procedure for determining relative isotopic concentrations of U^{235} , U^{236} , and U^{238} . An a.c. arc was used to excite the sample and correction factors were determined to correct for overlapping of the isotopic lines as well as for underlying weak unlisted uranium lines.

Two types of high resolution instruments have been used: the grating spectrograph usually in the higher orders and the Fabry-Perot interferometer with a grating or prism monochromator.

In the former case, the quality of the grating must be nearly perfect in order to produce sharp spectral lines and resolve with adequate definition structures like the mercury 2536 line shown in Figure 1b. The separation of individual components of the pattern is about 0.01A. The presence of spurious satellite lines must be nearly negligible in order to avoid interferences between neighboring isotope lines. The pattern demonstrates a resolving power of 750,000 or better.

Another typical pattern is the uranium 4244.37A line shown in Figure 1c. The lines excited in an electrodeless discharge tube were photographed in the sixth order of the Argonne 30 ft. spectrograph.¹⁹ The separation of U^{235} - U^{234} lines is about 0.05A. A direct photomultiplier trace of the U^{235} - U^{238} pair for the same line in the first order is shown in Figure 2.

The Fabry-Perot interferometer may also be used as the high resolution instrument



(Courtesy Argonne National Laboratory)

FIG. 1a. Li 6707 A group excited in a water cooled-hollow cathode tube and photographed in 4th order of the Argonne 30-ft grating spectrograph. The fine structure shift is 0.15 A. High wavelengths are to the right.

FIG. 1b. Hg 2536 A group excited in an air-cooled discharge tube and photographed in the 10th order of the Argonne 30-ft spectrograph. The pattern has a width of about 0.045 A and the separation of the strongest pair of lines is about 0.01 A. The various hyperfine components and isotopic lines are identified.

FIG. 1c. Isotope structure in U 4244.37 A line photographed in the 6th order of the Argonne 30-ft spectrograph. The concentrations of U^{234} , U^{235} , U^{236} and U^{238} were 18.17, 55.47, 18.51 and 7.85 per cent, respectively. The greater width of U^{235} line is due to the hyperfine structure. The spectrum was excited in an electrodeless discharge tube.

with a small grating or prism monochromator to select the limited wavelength region of interest. In this application the grating need not be of the same high quality described above.

A system used by Blaise²⁰ is shown in Figure 3. Light from the liquid air cooled hollow

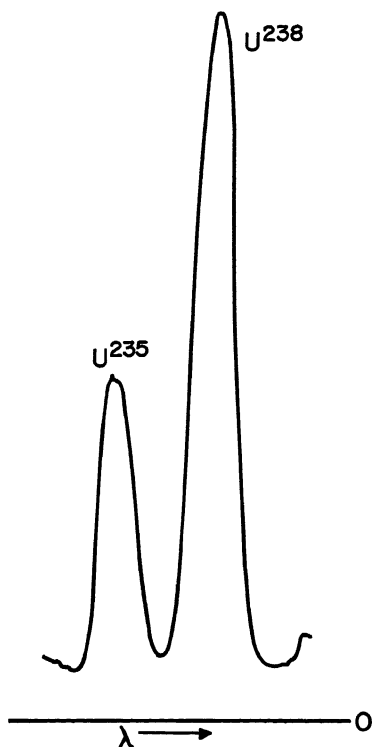


FIG. 2. Photomultiplier trace of U 4244.37 Å in 1st order of 30-ft spectrograph for a U^{235} concentration of 31.06 per cent. The lines were excited from uranium metal in a water cooled iron hollow cathode.

cathode, C, passes through a prism, P, which serves as an order sorter. Lens L1 focuses an image of the source on the slit F1 of the grating monochromator which allows the selected wavelength to pass through slit F2. Lens L2 focuses an image of the source midway between L2 and mirror M2, and lens L3 illuminates the interferometer, I, in parallel light while lens L4 focuses the fringes on the circular opening to the photomultiplier tube, T. The latter is cooled in liquid air to reduce dark current, thus allowing the photomultiplier to be operated at higher gain which in turn permits a reduction of the light source intensity resulting in still sharper lines and greater freedom from self-absorption.

The size of the circular opening before the photomultiplier tube is the same as the central fringe of the interferometer pattern after

magnification by L4. The output of the photomultiplier tube is sent to a cathode follower impedance matching amplifier and then to the recorder.

The interferometer fringes are scanned by gradually changing the pressure between the interferometer plates. This is accomplished by mounting the interferometer in a pressure chamber and slowly increasing or decreasing the pressure. The change in air density between the interferometer plates changes the index of refraction and the optical path length, thereby causing the interferometer to scan as many as several orders if desired. A large tank of compressed air or nitrogen connected to the chamber and controlled by a fine needle valve has been used to vary the pressure. For purposes of wavelength measurement the pressure change must be uniform. Another apparatus for more precise pressure control has been described by Blaise.²⁰

An alternative system using the scanning interferometer ahead of the monochromator has been described⁹ that provided a means of utilizing an internal standard beam which proved particularly useful for electrodeless discharge tubes.

The scanning Fabry-Perot provides re-

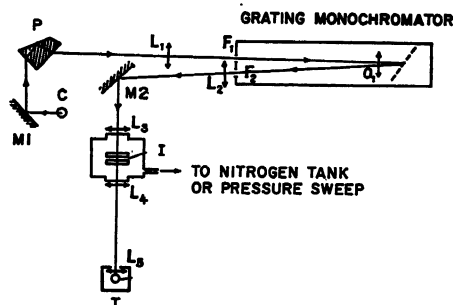


FIG. 3. Scanning Fabry-Perot spectrometer described by Blaise¹⁴. Light from a liquid air cooled-hollow cathode passes a prism order sorter and thence to a grating monochromator. The interferometer is illuminated in parallel monochromatic light. A liquid air-cooled photomultiplier tube observes the central fringe of the interference pattern. Scanning is accomplished by a gradual uniform pressure change in the interferometer chamber.

corder traces similar to that for the lead 5201A line shown in Figure 4. From the peak heights the relative concentration of the various isotopes can be calculated. In addition to the Pb 5201A line, the Pb 4058 line has also been used for isotope assay. The former line is preferable from the standpoint of self-absorption and the complexity of the Pb²⁰⁷ hyperfine pattern.

As an example of the concentration limit of the method a series of U²³⁵-U²³⁸ traces are shown in Figure 5 for the uranium 5027A line.²¹ Present in the pattern is a weak unshifted line *B*, whose intensity relative to the U²³⁸ line has been determined. The line *B* serves as a comparison line for U²³⁵ at very low concentrations and the U²³⁵/U²³⁸ ratio is calculated thus:

$$\frac{I_{U^{235}}}{I_B} \cdot \frac{I_B}{I_{U^{238}}} = \frac{I_{U^{235}}}{I_{U^{238}}}$$

where *I* is the intensity of the line indicated by the subscript and $I_{U^{235}}/I_{U^{238}}$ is proportional to the concentration ratio. In the trace of Figure 5 the U²³⁸ line has been attenuated by a large factor.

Table 1 shows some results of the optical method of isotope assay for uranium. The U²³⁵, U²³⁸ isotope pair for the 4244.37A line

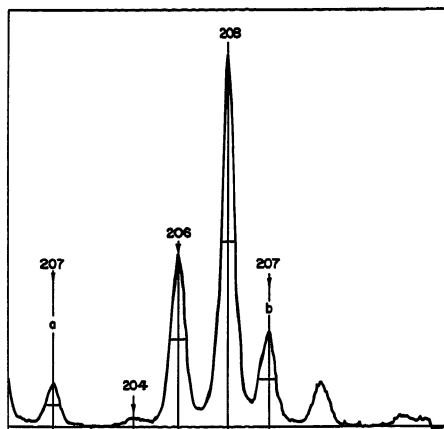


FIG. 4. Scanning Fabry-Perot spectrometer trace for Pb 5201 A by Blaise¹⁸. Pb²⁰⁷ has two hyperfine structure components a, b. From the peak heights the relative isotopic concentrations may be calculated.

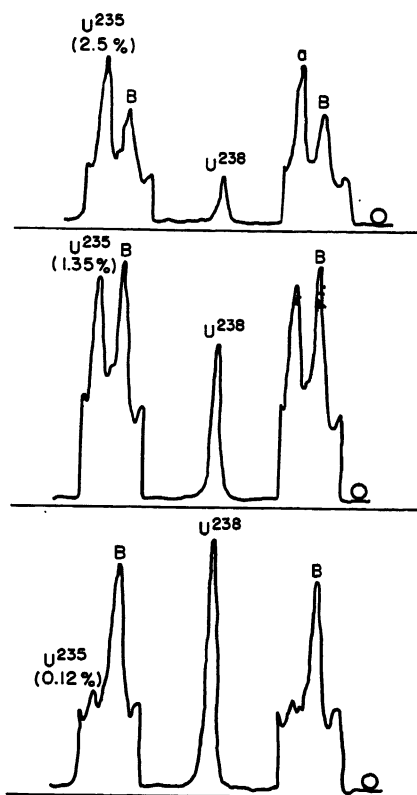


FIG. 5. Scanning Fabry-Perot spectrometer trace for U 5027 A for (a) 2.5 per cent U²³⁵, (b) 1.35 per cent U²³⁵ and (c) 0.12 per cent U²³⁵. The U²³⁸ line has been attenuated by several factors. The unshifted line *B* serves well as an internal standard line. This series of traces demonstrates a practical limit for the lower concentration.

was excited in a water cooled hollow cathode tube and resolved in the second order of the Baird 3 meter grating spectrograph. The isotope pair was scanned directly with a photomultiplier tube and slit.¹³

A comparison of mass spectrometric results with the optical results for lead is shown in Table 2. The scanning Fabry-Perot interferometer was used with the lead 5201A line for normal lead and 4058A line for the enriched samples.

The relative abundance of the mercury isotopes was determined utilizing the Hg 4046.6A line to determine the Hg¹⁹⁹/Hg²⁰¹ ratio. With this ratio known, the relative

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TABLE 1. REPRODUCIBILITY OF URANIUM ISOTOPIC DETERMINATIONS USING HOLLOW CATHODE EXCITATION

Sample A ^a			Sample B			Normal Uranium		
Trace No.	%U ²³⁵	Deviation from Av (v)	Trace No.	%U ²³⁵	Deviation from Av (v)	Trace No.	%U ²³⁵	Deviation from Av (v)
1	3.78	0.06	1	6.99	0.05	1	0.697	0.003
2	3.72	0.00	2	7.13	0.09	2	0.673	0.021
3	3.61	0.09	3	7.13	0.09	3	0.527	0.167
4	3.77	0.05	4	7.01	0.03	4	0.842	0.148
5	3.84	0.12	5	7.07	0.03	5	0.744	0.050
6	3.72	0.00	6	7.01	0.03	6	0.824	0.130
7	3.67	0.05	7	6.93	0.11	7	0.642	0.052
8	3.72	0.00	8	7.00	0.06	8	0.602	0.092
9	3.53	0.19	9	7.19	0.15			
10	3.82	0.10	10	6.91	0.13			
Av 3.72 3.72% ± 0.02% ^b			Av 7.04 7.04% ± 0.02% ^b			Av 0.694 0.694% ± 0.025% ^b		

^a Sample A Was a Synthetic Mixture of Uranium Oxides which Was Made to Contain 3.70% U²³⁵.

^b Calculated According to the Method of Least Squares $r_0 = 0.6745 [\Sigma v^2/n(n-1)]^{1/2}$ where r_0 = probable error in average, v = deviation from average, and n = number of traces.

TABLE 2. COMPARISON OF MASS SPECTROMETRIC AND OPTICAL SPECTROGRAPHIC RESULTS LEAD ISOTOPE ASSAY

		Pb ²⁰⁶ (%)	Pb ²⁰⁸ (%)	Pb ²⁰⁹ (%)	Pb ²¹⁰ (%)
Normal	Opt. Spec. ^a	52.35	25.15	1.35	21.15
	Mass Spec. ^b	52.3	24.8	1.4	21.5
Enriched Pb ²⁰⁶	Opt. Spec. ^c	16.6	64.9	—	18.4
	Mass Spec. ^d	16.55	64.93	0.172	18.35
Enriched Pb ²⁰⁸	Opt. Spec. ^c	87.0	2.94	—	10.1
	Mass Spec. ^d	87.97	1.99	0.089	9.97
Enriched Pb ²⁰⁷	Opt. Spec. ^c	30.6	7.76	—	61.6
	Mass Spec. ^d	31.9	7.73	—	61.06

^a Optical Spectroscopic Values by Jean Blaise¹⁸ Using the PbI 5201A Line (See Figure 4).

^b Nominal Values for Normal Lead by Ehrenburgh as Quoted by Steudel.²⁴

^c Opt. Spec. Values Using Pb4058A Line.⁹

^d Mass Spectrometric Values on the Same Sample Supplied by Stable Isotope and Production Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

concentration of the other isotopes was determined using the Hg 2536.5A line. The isotopes Hg²⁰² and Hg²⁰⁰ were determined directly from the intensity measurements. In the case of the odd isotopes one hyperfine

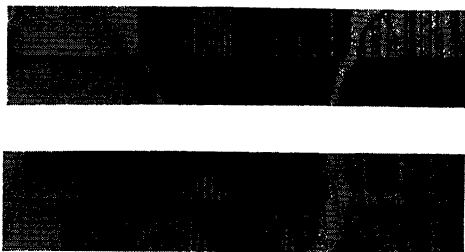
TABLE 3. ISOTOPE ASSAY FOR NORMAL MERCURY COMPARISON OF OPTICAL AND MASS SPECTROMETRIC RESULTS

Isotope Method	198	199	200	201	202	204
Opt. Spec.	10.1	18.1	22.4	13.9	29.2	6.33
Mass Spec.	10.1	17.0	23.3	13.2	29.6	6.70

structure component was measured and the total intensity calculated using theoretical intensity relationships. The 4046.6A line was scanned directly, photoelectrically in the fifth order of the 30 ft. spectrograph; the 2536.5A line in the tenth order. The results for normal mercury are shown in Table 3.

As an example of isotope shift in molecular band spectra and its use in isotope ratio determinations, the 1,0 and 0,1 bands of CuCl E system excited in an electrodeless discharge tube and photographed in the fifth order of the Argonne 30 ft. spectrograph are shown in Figure 6. The vibrational and rotational shifts are apparent.

The intensity of the band heads has been measured and used to calculate the relative isotopic abundances. In mixtures of isotopes



(Courtesy Argonne National Laboratory)

FIG. 6. Molecular spectra of CuCl for (a) 0,1 band of $\text{Cu}^{65}\text{Cl}^{35}$, (b) 0,1 band of $\text{Cu}^{63}\text{Cl}^{35}$, (c) 1,0 band $\text{Cu}^{65}\text{Cl}^{35}$, (d) 1,0 band of $\text{Cu}^{63}\text{Cl}^{35}$. In a mixture of Cu^{65} and Cu^{63} , the 0,1 band intensity is measured when the Cu^{65} concentration predominates; the 0,1 band when Cu^{63} predominates.

there is a certain amount of overlapping of bands which in cases like CuCl limits the number of isotopic components which can be determined simultaneously due to the complexity of the spectrum. In normal CuCl there are four isotopes present, resulting in the superposition of the bands for which a correction can be provided. The result of such an analysis for normal CuCl is shown in Table 4.

Broida *et al.*^{22, 23} have used C_2 and N_2 bands for determination of carbon and nitrogen isotopes, respectively. In these cases there is negligible overlapping of the band heads.

The optical method of isotope assay is possible as one result of the finest efforts in the science of optics. Where the grating is the high resolution component of the system, the burden of excellence rests with the ruling engine and its expert operation. For the interferometer the burden is shared by the skilled optician who makes the plates flat to $\frac{1}{60}$ th wavelength of green light and the coating expert who evaporates several alternate layers of materials on the plates, each carefully controlled in thickness.

The assays discussed were chosen as representative of the optical method utilizing both the grating and the interferometer as the high resolution instrument. A more comprehensive list of isotopes already determined is given by Brody and Tomkins.²⁵

TABLE 4. OPTICAL AND MASS SPECTROMETRIC VALUES FOR NORMAL COPPER AND CHLORINE

	Cu^{65}	Cu^{63}	Cl^{37}	Cl^{35}
Opt. Spec.	30.7 ± 0.2	69.3 ± 0.2	24.1 ± 0.1	75.9 ± 0.1
Mass Spec.*	31.06	68.94	24.6	75.4

* Nominal Values from Landolt-Börnstein, Zahlenwerte und Funktionen; 1. Band, Atom- und Molekularphysik; 5. Teil, Atomkerne und Elementarteilchen Springer-Verlag, Berlin, Göttingen, Heidelberg, 1952.

However, in general the same techniques can be applied to any element which exhibits a resolvable isotope shift provided the hyperfine structure is small or completely resolved.

REFERENCES

1. ROSE, J. L., GRAVATH, L. P., *Phys. Rev.*, **39**, 1017 (1932).
2. MOORE, KENNETH R., *Phys. Rev.*, **45**, 132 (1934).
3. BACHER, R. F. AND SAWYER, R. A., *Phys. Rev.* **47**, 587 (1935).
4. HARRISON, GEORGE R., STURGIS, NEVILLE, DAVIS, SUMNER P., AND YAMADA, YAHIKO, *J. Opt. Soc. Am.*, **49**, 206 (1959).
5. PIERCE, A. KEITH, *J. Opt. Soc. Am.*, **47**, 6 (1957).
6. JACQUINOT, P., AND CH. DUFOUR, J., *Rech. C.N.R.S.*, **2**, 91 (1948).
7. JACQUINOT, P., *J. Opt. Soc. Am.*, **44**, 761 (1954).
8. JACQUINOT, P., AND CHABBAL, R., *J. Opt. Soc. Am.*, **46**, 556 (1956).
9. BRODY, J. K., TOMKINS, F. S., AND FRED, M., *Spectrochimica Acta*, **8**, 329 (1957).
10. PENSELIN, SIEGFRIED AND STEUDEL, ANDREAS, *Z. Phys.*, **142**, 21 (1955).
11. GIACOMO, P., *C. R. Acad. Sci. Paris*, **235**, 1627 (1952).
12. JARRETT, A. H., *Nature*, **169**, 790 (1952).
13. BRODY, JAMES K., *J. Opt. Soc. Am.*, **42**, 408 (1952).
14. SHÜLER, H., AND GALLNOW, H., *Z. Physik*, **93**, 611-619 (1935).
15. BLAISE, JEAN, *Ann. Phys.*, **3**, 1019 (1958).
16. BRODY, J. K., FRED, M., AND TOMKINS, F. S., *Spectrochimica Acta*, **6**, 383 (1954).
17. TOMKINS, FRANK S., AND FRED, MARK, *J. Opt. Soc. Am.*, **47**, 1087 (1957).
18. SAUNDERSON, J. L., Reported at Opt. Soc. Am. Meeting, October 8-10, 1959, Ottawa, Canada.

EMISSION SPECTROSCOPY—LIGHT

19. TOMKINS, FRANK S. AND FRED, MARK, *Spectrochimica Acta*, **6**, 139 (1954).
20. BLAISE, J., *Ann. Phys.*, **3**, 1019 (1958).
21. ARTAUD, J., BLAISE, J., GERSTENKORN, S., Second United Nations International Conference on the Peaceful Uses of Atomic Energy, **15**, 328 (1958).
22. BROIDA, H. P., AND CHAPMAN, M. W., *Anal. Chem.*, **30**, 2049 (1958).
23. FERGUSON, R. E., BROIDA, H. P., *Anal. Chem.*, **28**, 1436 (1956).
24. STEUDEL, A., *Z. Phys.*, **133**, 438 (1952).
25. BRODY, J. K., AND TOMKINS, F. S., Second International Conference on Peaceful Uses of Atomic Energy (1958).

JAMES K. BRODY,
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JEAN BLAISE

MICROPHOTOMETERS OR MICRODENSITOMETERS

In attempting to make any kind of quantitative measurement in photographic spectrochemical analysis, it becomes necessary to measure the blackness of the spectral lines on the plate. Usually these measurements involve areas of the emulsion of the order of 5000 to 25,000 square microns (.005 mm² to .025 mm²), as contrasted to the several square millimeters measured in normal photographic photometry, hence the appellation microphotometer or "microdensitometer". Strictly speaking, however, it would be more appropriate to apply the latter term only to instruments that record densities directly. In addition, because a microphotometer must measure a small area of the plate, it should have features not required of photometers for larger areas, particularly:

- (1) higher sensitivity and greater speed in the measuring circuit;
- (2) means of identifying the area to be measured;
- (3) mechanical means of aligning the line parallel to the detector slit;
- (4) mechanical means for moving rapidly to the line to be measured and then for

scanning slowly, steadily, and reproducibly, to obtain the same deflection (in a non-recording instrument);

- (5) means of eliminating "scattered" light.

Optical Systems

Schwarzschild and Villiger¹ discovered that if one illuminated a larger area of emulsion than the spectral line itself, light scattered from adjacent silver grains and from optical surfaces could result in a transmission reading higher than it should be. The effect is detectable for dense lines only. A line that should show a transmission reading of 0.1 % may indicate 1.5 %.

The Schwarzschild-Villiger effect has two practical results: (1) a Hurter and Driffield characteristic curve of density plotted as a function of illumination may begin to show a "shoulder" at a density of perhaps 1.5 (transmission = 3.1 %) and may become completely flat above 1.8 ($T = 1.6$ %). (2) Lines in the density range 1.5 to 1.8 will have a variable density, depending on any variations in the blackness of lines in the surrounding illuminated area. A little care in the design of the optics will reduce the effect to the point where the shoulder begins at 1.8 to 2.0 and the curve levels off at 2.3 to 2.5. This is usually adequate, since in most quantitative spectrochemical analysis lines are selected to have transmissions above 2.0 %, or even 5 %, merely to obtain the desired 1 or 2 % in reading accuracy. It should be remembered, however, that because of the effect, characteristic curves obtained on most commercial microphotometers will not match the curves shown by manufacturers of photographic emulsions, which are derived from sensitometric strips. Such photometric measurements on large areas of emulsion will give straight line characteristic curves up to densities of 4 or 6.

The requirements of an optical system which will eliminate the Schwarzschild-Villiger effect tend to be antithetical to the needs for a system to view a large area of the

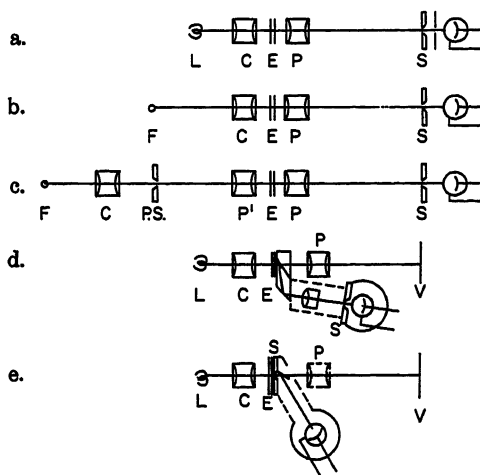
plate for ready identification of lines. The following systems have been used.

Simple Plate Projection. A large area of the plate is illuminated and is projected directly on a viewing screen containing a detector slit (Fig. 1a). While such systems suffer badly from scattered light and in some instances can be markedly affected also by variations in the level of room illumination, these effects are usually of little handicap so long as the operator restricts his measurements to lines in the transmission range above 3%, which is good practice for adequate precision. In addition, lines are readily identified. Bausch & Lomb, Baird-Atomic, and several European manufacturers employ such arrangements.

Slit Illumination. A straight line filament is projected directly on the plate, at reduced magnification, say, $\frac{1}{10}$ size (Fig. 1b). The filament image is projected directly onto the detector slit, or (Fig. 1c) a pre-slit with opaque jaws is projected on the plate.

System (b) permits density readings to 3.0 or above. It is used in the Hilger & Watts and Leeds & Northrup instruments. In the Hilger, the operator inserts an auxiliary lens when he wishes to view the plate. System (c), if the slit image is reduced narrower than the width of the spectrum line, will give readings to densities of 5.0 or more. It was used in the Moll recording densitometer by Kipp and Zonen and has been supplied by Jarrell-Ash in special cases requiring high-density readings.

Filter Jaw Pre-slits. Zeiss and Jarrell-Ash have utilized modifications of the design of Fig. 1c, in which the traditional opaque jaws were replaced by jaws of colored filter glass. These reduce the level of illumination of the surrounding area to 5 to 15% of the line illumination, thus reducing scattered light by the same proportion. A second filter complementary to the first can be placed behind the detector slit, still further reducing scattered light. National Spectrographic Laboratories has utilized



L = Lamp; F = Line Filament; C = Condensing Lens; P.S. = Pre-slit; P' = Pre-slit Projection System; E = Emulsion; P = Projection lens, opaque viewing; S = Screen and slit; V = Translucent viewing screen.

FIG. 1. Optical projection systems for microphotometers.

- (a) Simple projection.
- (b) Line filament projected on emulsion.
- (c) Pre-slit projected on emulsion.
- (d) Mirror pre-slit behind emulsion.
- (e) Slit at the emulsion.

crossed Polaroid filters in a similar arrangement, but this is not so effective, because the scattered light is depolarized.

Slit Mirror. Jarrell-Ash (Fig. 1d) has used a 40–50 micron mirror coated on the face of a cemented rhomb just below the plate, to accept only the light from the immediate vicinity of the line for the measuring beam, while utilizing all of the illumination of the remainder of the plate for the projected screen image.

Slit at Emulsion. Applied Research Laboratories has used a scanning slit placed directly behind the emulsion as a means of diverting the light to be measured (Fig. 1e). The slit is inserted in the field of view only when a line is actually being scanned. At other times the whole field of view is projected. The arrangement not only greatly reduces the Schwarzschild-Villiger effect, but also results in a slightly steeper slope for the characteristic curve because the measure-

ments are strictly specular. (Specular densities, obtained by measuring the transmitted light within only a few degrees from the normal to the surface, are appreciably higher than diffuse densities, obtained by measuring the light transmitted throughout a wide cone of 20 to 80° from the normal.) Since inserting the slit obscures the field of view, the line to be scanned is first brought to a fiducial mark on the projection screen. There are practical problems to this optical system, particularly the possibility of scratching the emulsion and the difficulty of maintaining the position of the slit, so that the line being measured is positively identified.

Measuring Circuits

As in all photometric instruments, the measuring circuit of a microphotometer must be highly stable. The operator would like to be able to set his "clear plate" reading to 100 % (or 0), and his opaque reading to 0 % (or 100), and feel that the readings will remain constant for 5 to 15 minutes while he measures a series of lines. At the same time, the measuring system must be able to give full-scale response for at least 5000 square microns (a slit of, say, 10 microns $\times$ 0.5 mm) and have a response time of better than 2 seconds, to permit reasonably rapid readings. With the improvement in photodetectors, measuring circuits have improved in performance, but increased in electronic complexity.

Thermopile-Galvanometer. Early microphotometers were forced to rely on thermoelectric detectors. One of the earliest commercial microphotometers, the Moll² of Kipp and Zonen, used a vacuum thermocouple as detector. Because of its low impedance, the thermocouple had to be connected directly to a low-impedance galvanometer. When the instrument was used as a recording microphotometer, the galvanometer mirror imaged a brightly illuminated spot on a rotating drum carrying photographic paper. The thermocouple had

disadvantages. High sensitivity and rapid response were difficult to achieve simultaneously. The thermopile was temperature-sensitive, and since it responded to all wavelengths, it required either a filter or highly corrected optics to obtain definition and resolution. The photographic paper was also slow and inconvenient.

Barrier Layer Photocell-Galvanometer. The barrier layer photocell was insensitive to temperature. It permitted better sensitivity and more rapid response, and it was more rugged. Because of its higher impedance, a less sensitive and faster taut suspension galvanometer could be used. A potentiometer used as an Ayrton shunt permitted the full scale deflection to be set.

In the early Hilger, Bausch & Lomb, and Zeiss microphotometers the galvanometer deflection was measured by a projected spot moving along a 500-mm scale. This meant that the operator had to shift his position as the galvanometer deflected, to avoid parallax. Zeiss, Hilger, Jarrell-Ash, Applied Research Laboratories, and National Spectrographic Laboratories later utilized a system which effectively projected a moving millimeter scale across a fixed fiducial mark on a viewing screen.

Phototube-Amplifier. Barrier layer photocells have too low an impedance to permit amplification. In its early instruments Applied Research Laboratories used a phototube, amplifier, and meter circuit. In later instruments the meter was replaced by the projected galvanometer scale mentioned above. In the recording microphotometer designed by Knorr and Albers³ and built by Leeds & Northrup, a phototube and stabilized amplifier actuated a Speedomax strip chart recorder, to give the first directly-linked microphotometer tracing. Later Jarrell-Ash Company utilized a multiplier phototube, in a circuit compensated against voltage fluctuations by a second photomultiplier viewing the lamp directly, in their recording microphotometer. A similar circuit

was later applied to their non-recording instrument, driving a servo-head that carries a scale which is projected on the viewing screen, eliminating the galvanometer. In a "Scalock" arrangement, the servo-head can be arrested at its minimum deflection, relieving the operator of the necessity for constantly observing the fast-moving scale. A similar servo system is now being used by Applied Research Laboratories.

"Null" Circuits. The early Baird-Atomic microphotometer employed a null circuit. The line was scanned across the slit until a minimum deflection was obtained. A variable-density wedge in a reference optical path was then adjusted until the current at minimum deflection was exactly matched. The reading of the scale of the wedge gave the density directly. The arrangement, while theoretically sound from the standpoint of electronic stability, proved too cumbersome and slow in actual operation because of the dual manipulation required for each reading. The circuit has since been mechanized, so that the operator merely scans across the line, as in equivalent instruments.

Scale Readings

In every microphotometer measurement, although only one reading is actually tabulated, three others are implied, as indicated by the equation

$$\frac{J}{J_0} = \frac{D_1 - D_0}{D_{100} - D_0}$$

where J_0 represents the illumination on the detector slit without the line, J with the line, and D_1 , D_0 and D_{100} represent the scale readings, respectively, for the line, for complete opacity, and for "clear plate". If the microphotometer is stable to 0.1 or 0.2% over the period of reading, the operator assumes that D_{100} and D_0 remain constant. He should always adjust the clear plate and zero readings just before starting a series of measurements, and check the settings after finishing. The clear plate reading is some-

times taken at a portion of the plate which was completely masked, but preferably it should be at a spot which typifies the general fog level of the plate, exclusive of spectral background.

Characteristic Curve of a Photographic Emulsion

All photographic work depends on the fact that a developed image becomes proportionately blackened at the areas that have received the greatest illumination. In spectrochemical analysis, the response of the photographic emulsion must be determined quantitatively, since we hope to measure the relative intensities of analytical and internal standard lines to a precision approaching 1%. This requires the calibration of the emulsion for the wavelengths being used, from measurements on an exposure taken through a stepped sector, stepped filter or other device which varies the intensity of the light incident to the emulsion in a precisely known way.

Typical readings, obtained from an exposure through a stepped sector with a 2:1 ratio (each successive step transmits twice as much light as the preceding step), are shown in Table 1 and are plotted in Fig. 2. Before starting the readings, the microphotometer scale was set to zero when the light path was completely obstructed and to 100 for a clear area of the emulsion. Four different methods of plotting a characteristic

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Deflection D	Opacity $100/D$	Density (d) $\text{Log} \left(\frac{100}{D} \right)$	Black- ening (B) $100 - D$	Seidel (S) $\text{Log} \left(\frac{100}{D} - 1 \right)$	$-\log D$
95.0	1.05	.012	5.0	8.70-10.0	1.99
80.1	1.25	.10	19.9	9.40-10.0	1.90
47.8	2.09	.32	52.2	0.04	1.68
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4.6	21.7	1.34	95.4	1.32	0.66
1.02	98	1.99	99.0	1.99	0.01

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1.02	98	1.99	99.0	1.99	0.01

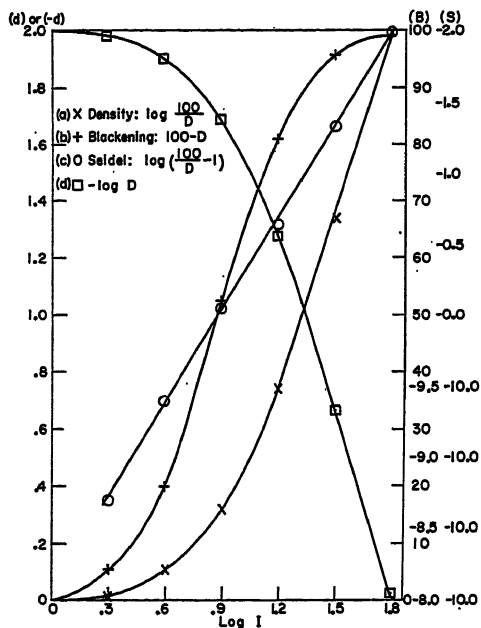


FIG. 2. Methods of plotting the response of the photographic emulsion.

curve have been used. These are shown in Fig. 2 and are described briefly below:

Density. The density is defined as $\log (J_0/J)$, that is, the logarithm of the ratio obtained by dividing the incident light by the light transmitted by the line. This is obviously measured by $\log D_{100}/D = \log 100 - \log D = 2 - \log D$. The plot of density against $\log I$, where I represents the intensity of the light used in the original exposure, produces the classical Hurter and Driffield curve used in photographic photometry (Fig. 2, a). Unfortunately, the plot is highly curved at the region of light lines, which makes it difficult to use for trace elements. Another disadvantage is that D can be plotted directly on semilogarithmic paper only if the paper is turned upside down.

Blackening. The blackening is simply a direct plot of the deflection, on a linear scale, against $\log I$ (Fig. 2, b). In this instance, however, the microphotometer scale is reversed, so that the clear plate reading is zero and complete opacity reads 100. This gives

directly the readings shown in Column (4) of Table 1. This function has been preferred by B. F. Scribner of the Bureau of Standards and by Sawyer and Vincent of University of Michigan because it makes it easier to instruct technicians in routine work, since the reading increases with concentration. However, there is really no straight line portion to the curve.

The Seidel Function. The Seidel⁴ function is defined as $\log ((1/T) - 1) = \log ((D_{100}/D) - 1)$. When this function is plotted against $\log I$ (Fig. 2, c), the straight line section continues to much higher values of D , where the classical density function develops a severe "toe". The Seidel function is clearly superior for trace element work.

Negative Density or Seidel. To obtain the traditional Hurter and Driffield or Seidel functions requires plotting D on a reverse logarithmic cycle. Since this involves turning normal graph paper upside down, it is common to plot D downward, i.e., $-\log D$ (Fig. 2, d). This method of plotting leads to curves which are the mirror images of the Hurter and Driffield or Seidel curves.

The recent trend is toward use of the negative Seidel function as most convenient and best adaptable to the measurement of light lines. For an exhaustive treatment of photometric data reduction the reader is referred to the article by C. Feldman, reference 5.

It is possible to graduate the scale of the microphotometer to read any of these functions directly, but there seems little point to this, since the same curve is obtained if the appropriate graph paper or calculating board scale is employed to plot the deflections. Most operators find a linear scale easier to read quickly.

Non-recording and Recording Microphotometers

Many microphotometers are used exclusively for quantitative measurements, scanning only the lines of interest to determine the minimum deflection. The me-

mechanical motions required in such a "spotting" or non-recording microphotometer are:

- (1) a rotation or tilt adjustment to align the spectrum lines parallel with the detector slit;
- (2) rapid transverse movement from spectrum to spectrum;
- (3) rapid longitudinal motion along the spectrum to the desired line;
- (4) a slow, steady scan across the line.

In a recording microphotometer, the latter two motions are combined into one and motorized. A range of speeds from about 0.05 mm to 25 mm/minute is normally provided; the most useful speed is normally 0.25 mm/minute. Paper speeds of 1 to 4"/minute are common for the recorder. Recording microphotometers are used if it is necessary to determine the relative density and, sometimes, the spacing of many lines in a spectrum, or if background corrections or line contours are important.

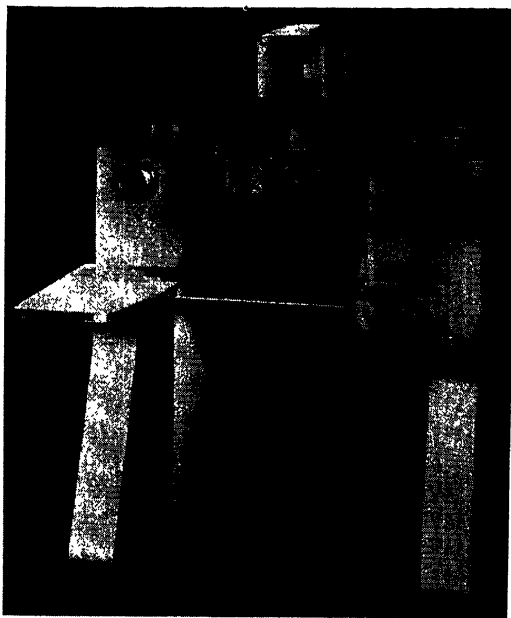
Comparator Microphotometers

Applied Research Laboratories first introduced a combined comparator-microphotometer, which permitted not only quantitative measurements but also projected a reference spectrum beside the unknown, for qualitative analysis, or merely for ease in identifying the lines to be measured in quantitative work. Jarrell-Ash, National Spectrographic Laboratories, Hilger & Watts, and Optica now make such combination instruments. Figure 3 is typical.

Comparators

For qualitative analysis only, Hilger & Watts has supplied for many years the Judd Lewis Comparator, a device for holding and illuminating an unknown and reference plate, with a comparator microscope for examining the two images side by side at 10 $\times$ magnification.

Hilger & Watts, Jarrell-Ash, National Spectrographic Laboratories, and Steinheil



(Courtesy of Jarrell and Company)

FIG. 3. A typical comparator microphotometer.

manufacture double projectors for qualitative or visual quantitative analysis only.

Measuring Microscopes

The best commercial microphotometers have a precision of linear measurement good only to 20 or 30 microns. For precise wavelength determinations, a precision of at least 1, or even 0.1, micron is required. Such precision is obtained only with a measuring microscope. Such instruments are manufactured by Gaertner Scientific Corporation, D. W. Mann, Paul McPherson and Hilger & Watts.

Line Widths

Because of the restricted latitude of photographic emulsions and self-reversal of the lines in the source itself, a single spectrum line can scarcely be used over a concentration range greater than 500 or 1000. In some analytical work, as in mineralogy, it may be desirable to cover a wider concentration range. Junkes and Salpeter⁶ have worked out a technique dependent on effective line

width, which covers a much greater concentration range.

REFERENCES

1. SCHWARZSCHILD, K. AND VILLIGER, W., *Astrophys. J.*, **23**, 287 (1906).
2. MOLL, W. H. J., *Proc. Phys. Soc. (London)*, **33**, 207 (1921).
3. KNORR, H. V. AND ALBERS, V. M., *Rev. Sci. Inst.*, **8**, 183 (1937).
4. SEIDEL, W., reported in H. Kaiser, *Spectrochimica Acta*, **2**, 1 (1941).
5. Chapter on "Photographic Photometry in Spectrochemical Analysis" in "Methods for Emission Spectrochemical Analysis," American Society for Testing Materials, Philadelphia (1957).
6. JUNKES, J., S.J. AND SALPETER, E. W., S.J., "Ricerche Spettroscopiche," Vol. 2, No. 5, Specola Vaticana, Citta del Vaticano (1958).

R. F. JARRELL

MICROPHOTOMETRY: APPLICATION TO QUANTITATIVE SPECTROCHEMICAL ANALYSIS

In quantitative emission spectrochemical analysis, the chemical concentration of a given element is determined by measuring the intensity of one of its spectral lines relative to the intensity of a line of the "internal standard" element. The latter is an element which is present in the same concentration in all samples and standards. This intensity ratio is then converted to a concentration figure with the aid of an analytical curve previously prepared from synthetic or analyzed samples. When the spectrum is observed photographically, the intensity ratio is measured with a microphotometer or "densitometer," which is capable of measuring the per cent transmittance (%*T*) of very small areas of photographic film (e.g. 10–20 μ $\times$ 0.5–2.0 mm). Since the relationship between the %*T* of a developed image and the average line intensity which produced it is very complicated, it is necessary to prepare an empirical "calibration curve"; i.e. to measure the transmittance of the developed film after its exposure to a set of

light signals of known relative intensity for a fixed period of time. This calibration curve is then used to convert %*T* readings made with a microphotometer into intensity or log intensity values, which are related directly to chemical concentrations.

The shape of the calibration curve depends on the properties of the emulsion itself, including its age and history before exposure. It is also affected to various degrees by the wavelength of light used, the duration and intermittency of exposure, the conditions of photographic development and the slit-width and general optical design of both the spectrograph and the microphotometer. An intensity ratio obtained by referring measured %*T* values to such a curve is accurate only if the sample spectrogram was produced and measured with the same instruments, procedures and materials as were used to produce the calibration curve.

Techniques of Emulsion Calibration

The most direct approach to this problem is the use of a stepped intensity reducer (usually a stepped evaporated metal-on-quartz filter or rotating stepped-sector wheel; see Figure 1) at the stigmatic position of the spectrograph or, if physically possible, immediately in front of the plate or film. The spectrum of a light source having low spectral background, such as an iron arc, is photographed through this reducer. In the resulting spectrogram, each spectral line shows a stepwise variation of %*T* along its length. The %*T* of each step of a given line is measured with a microphotometer. Some function of %*T* (usually optical density *D* or Baker-Sampson (Seidel) function Δ , where $D = 2 - \log \%T$ or $\Delta = \log[(100/\%T) - 1]$) is then plotted against the known relative transmittance of the corresponding step of the intensity reducer. This method is illustrated in Figure 2, using optical density *D*.

The use of this approach involves several practical disadvantages, however. It is difficult to achieve the necessary vertical uni-

formity of illumination over the entire height of a five-step reducer. In addition, there is no objective way to average the results of several exposures when this method is used, so that the calibration curves obtained may not accurately represent the average response of the system at all density levels.

These difficulties have given rise to the "preliminary curve" approach, which goes far toward solving both of them. In this case, exposures are made through an intensity reducer which has only two steps; vertical uniformity of illumination is thus more easily attained. Several exposures are made at various intensity levels. In each of the resulting spectrograms, each line has a "weak" and a "strong" step. Some function of the % T reading for the weak step of a given line is then plotted against the same function for the strong step. Pairs of readings for a given spectral line obtained from separate exposures may be plotted on a common graph to give the "preliminary curve"; in fact, the data usually can be included from all lines over a narrow (~ 100 Å) spectral range. It has been found empirically that when the function used is the Baker-Sampson (Seidel) function $\Delta = \log[(100/\%T) - 1]$, the preliminary curve is a straight line; its most probable slope and intercept can thus be calculated by statistical methods. (This is not the case when % T itself or $D = 2 - \log \%T$ is used.) In the preliminary curve illustrated in Figure 3, the ordinate and abscissa scales are proportional to Δ but have been calibrated in terms of % T to avoid the necessity for calculating a Δ value for each observed % T . Point 1 in Figure 3 represents a spectral line image which gave transmittance readings of 36 % T and 12 % T on its weak and strong steps, respectively.

To construct the calibration curve, a point near the upper end of the preliminary curve (e.g. point A) is selected arbitrarily. The % T values shown for this point on the "Δ weak" and "Δ strong" axes (25 % T and 6.5 % T in

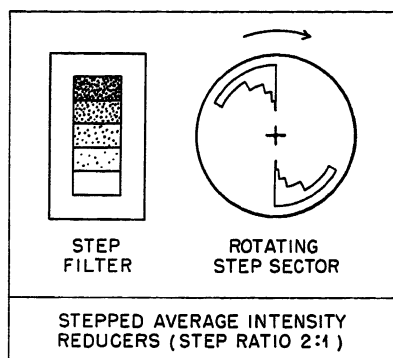


FIG. 1

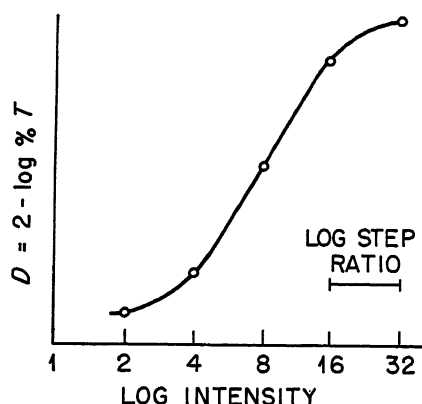


FIG. 2

this case) are noted. On a separate plot of % T vs. log relative (spectral line) intensity, the % T value read on the "Δ strong" axis is plotted at an arbitrary point at the right side. The % T value read on the "Δ weak" axis is then plotted to the left of the first point, at a distance equal to the logarithm of the step ratio of the intensity reducer used (see Figure 4). In this case, the step ratio is assumed to be 2.00.

Going back to the preliminary curve, the process is now repeated; the "Δ weak" value just used now is regarded as the "Δ strong" of a new pair. This value (25 % T) is located on the "Δ strong" axis, followed to the preliminary curve (point B) and a corresponding new "Δ weak" (61 % T in this case) located on the "Δ weak" axis. This % T value is now plotted at a similar interval to the

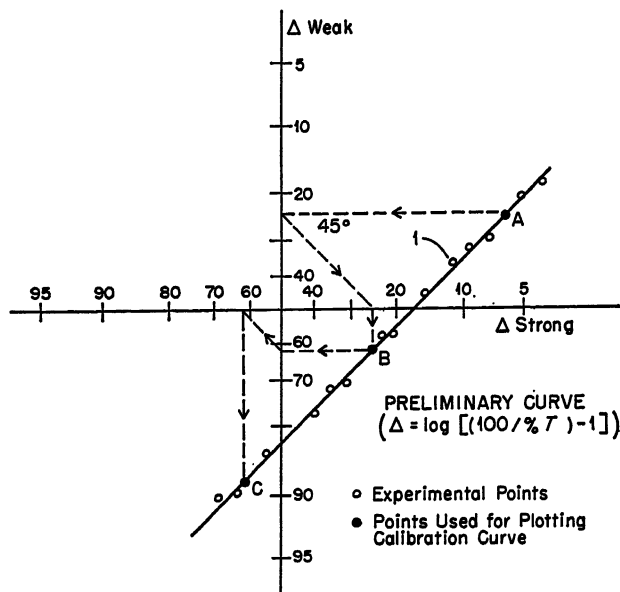


FIG. 3

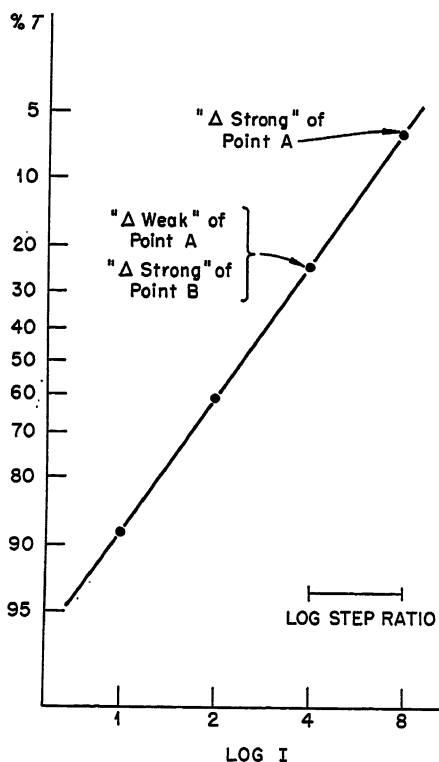


FIG. 4

left of the previous one. The process is continued until the $\%T$ scale has been covered. The dotted line in Figure 3 shows the graphical equivalent of this procedure. The result is a calibration curve which describes the response of a given spectrograph-microphotometer pair to a given emulsion at a given wavelength. If desired, the calibration curve can be converted into a "ruler" for reading relative intensity directly from the chart of a recording microphotometer.

In practice, it is often necessary to measure and correct for spectral background before calculating line intensity ratios, especially when line/background ratios are low (<5).

Detailed procedures for using microphotometers in spectrochemical analysis may be obtained from Method E-116-56T in the book "Methods for Emission Spectrochemical Analysis," published by Committee E-2 of the American Society for Testing Materials, Philadelphia, Pennsylvania, (1957).

CYRUS FELDMAN

MODERN SPECTROGRAPHS AND DIRECT READER SPECTROMETERS*

When a sample of material is properly excited by an electrical spark or arc, each element comprising the sample emits certain specific predictable wavelengths of light. Emission spectrochemical instruments detect these wavelengths of light for the elements of interest and by measurement of the intensity determine the per cent concentration of the elements in the sample.

The diagram (Figure 1) illustrates this principle of operation. The light emitted from the sample enters the instrument through a narrow vertical slit. The 3-meter concave grating separates the light by reflecting each wavelength at a different angle. This light is brought to focus at the focal curve as a spectrum line. The spectrum lines can be measured photographically or by electronic means using photomultiplier tubes. Spectrographs employ the photographic techniques. Direct reading spectrometers employ photomultiplier tubes.

The Spectrograph. The photographic technique is inherently more versatile than direct reading, whereas the latter is faster and more precise.

The photographic plate of the spectrograph records all the spectrum lines emitted (within range of the photographic emulsion and wavelength setting). The locations of the spectrum lines indicate which elements are present in the sample. Thus, contaminating elements or specimens of unknown material may be quickly identified. Quantitative analysis involves measurement of the optical intensity of the spectrum lines of interest. About 30 minutes is usually required for a quantitative analysis of about 5 elements (from excitation of the sample to reporting results). The time per sample can be reduced by accumulating samples and analyzing many on one photographic plate or film.

* Compiled from materials supplied by Baird-Atomic.

Typical of modern instrumentation, Figure 2 illustrates the Baird-Atomic spectrograph which employs a concave grating of 3-meter focal length in a modified Eagle mounting. In 1882 Rowland demonstrated the formation of high quality spectra by positioning the entrance slit, concave grating and photographic plate on the circumference of a circle with a diameter equal to the radius of curvature of the grating. In the Eagle mounting (1910) the slit and plateholder are maintained at a fixed position relative to one another on the Rowland circle. To bring the various regions and orders of the spectrum onto the plate, the grating is rotated and moved toward or away from the slit which has the effect of rotating the Rowland circle about the slit axis. The plateholder must be rotated about the slit axis in order to remain on the Rowland circle. Since the plateholder is close to the slit the angles of incidence and diffraction are nearly equal, the necessary condition for minimum aberration and maximum spectral definition.

Direct Reader Spectrometer. Figure 1 also shows the arrangement of instrumental components for direct reading analysis. In direct reading analysis, photomultiplier tubes are used to measure the intensity of light instead of photographic plates or film. Exit slits are carefully positioned on the focal curve so as to pass the specific wavelengths of the unknown elements of interest and the internal standard wavelength. A photomultiplier tube is positioned behind each exit slit to convert the light to electrical energy. During the exposure period the electrical output of the phototube is collected in the form of a voltage on a capacitor. At the end of the exposure, the voltages accumulated on the capacitors are a measure of the element concentrations analogous to the photographic procedure. That is, the voltage ratio between each unknown element capacitor and the internal standard capacitor is related to per cent concentration in a manner similar to

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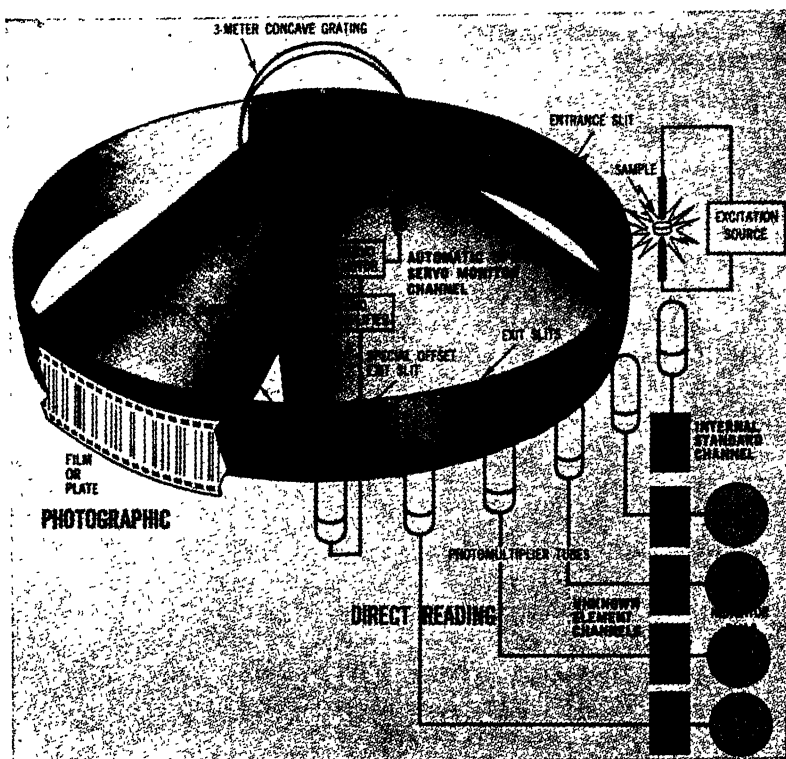


FIG. 1. Diagram of the principles of operation of the optical emission spectrophotometer (photographic) and the direct reader spectrometer (electric).

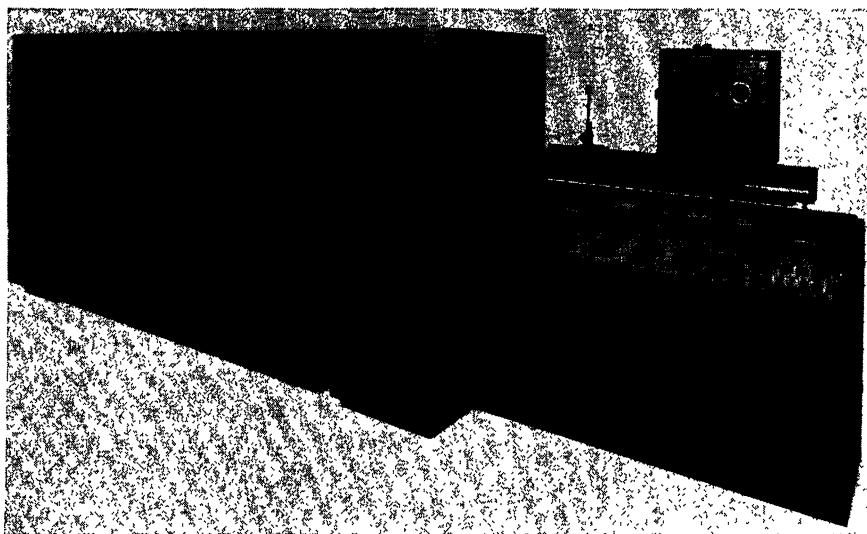


FIG. 2. Baird-Atomic Spectrograph with concave grating of 3-meter focal length in a modified Eagle mounting.

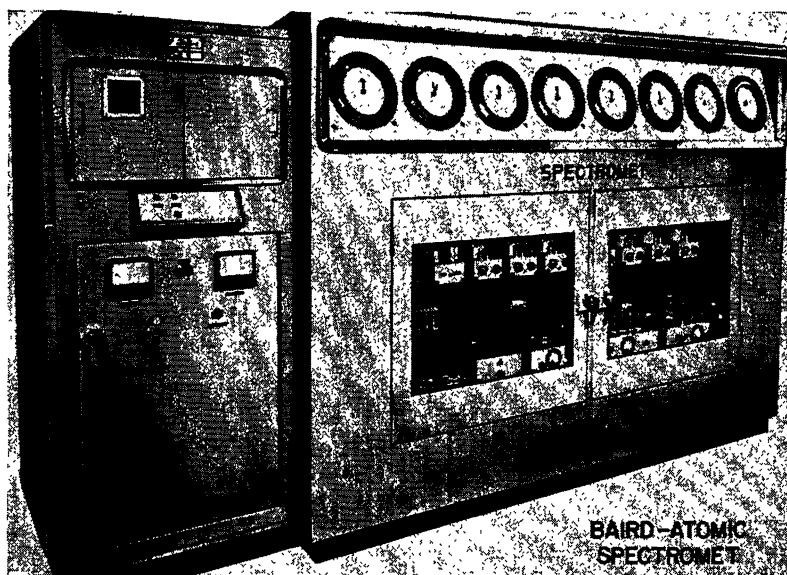


FIG. 3. Baird-Atomic Spectrometer direct reader spectrometer for rapid metallurgical analyses of eight elements simultaneously.

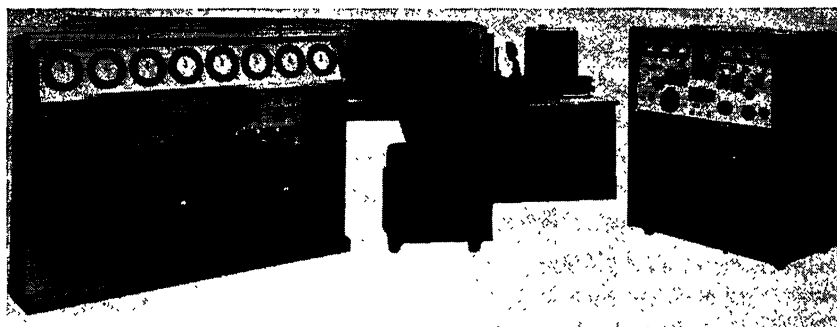


FIG. 4. Baird-Atomic Research Direct Reading Spectrograph with Spectrosource (right).

the use of optical intensity ratios in the photographic method.

The voltage ratios are measured and presented directly on indicator dials or on a strip chart recorder in less than one minute. The spectrometer shown in Figure 3, is an instrument of this type especially designed for rapid routine metallurgical analyses. The great advantages over the photographic technique lie in the fact that photomultiplier tubes can accurately measure light intensity with a relative range of 1:10,000, whereas the photographic range is 1:10 between the

lightest and darkest spectrum line that can be used on the plate. Furthermore, photographic emulsion calibrations are eliminated. In Figure 4 the Baird-Atomic Research Direct Reading Spectrograph is shown. Conversion from photographic to direct reading is accomplished in a few minutes; precise slit setting is accomplished electronically, and an automatic optical series continuously maintains spectrum lines in correct alignment during direct reading.

Also a logarithmic measuring scale and the Baird-Dow readout system are used. Because

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of the nature of the inherent precision of the emission spectrochemical approach, a logarithmic presentation of the results is desirable. It is commonly recognized that the precision involved is constant as a per cent of the amount present over a wide concentration range, especially above 0.1 % of element concentration. For example, the standard deviation for the element chromium in steel is about 1 % of the concentration present from 40 % to something like 1 %. Between about 1 % and 0.1 %, the precision worsens only gradually. This is summarized in Table 1.

TABLE 1

Chromium Present, %	Coefficient of Variation, %	Absolute Error (One Sigma), %
30	1	± 0.3
20	1	± 0.2
10	1	± 0.1
5.0	1	± 0.05
1.0	1	± 0.01
0.5	1.5	± 0.0075
0.1	4.0	$\pm .004$

A logarithmic scale, for example a slide rule, has the same type of inherent reading precision. That is, as the numbers decrease,

TABLE 2

Users	Uses	Users	Uses
<i>Metal Producers</i>		<i>Railroads, Truckers, and Diesel Engine Operators</i>	monitoring impurities in lubricating oil as preventative maintenance technique
Steel Plants	control of melting		analysis of metals and other purchased material
Iron & Steel Foundries	typing and sorting scrap		service failure investigations
Non Ferrous Foundries	certification of material		trace and minor elements in soils, plants, and fertilizers
Aluminum & Magnesium Refineries	slag analysis		minor elements in blood and human tissue
Lead & Zinc Smelters		<i>Agriculture & Public Health Agencies</i>	contaminants in air and stream pollution
Copper Producers			
Secondary Metal Producers			
<i>Metal Fabricators</i>		<i>Research Laboratories</i>	
Missiles and Aircraft Producers	analysis of purchased material	Industrial	investigation and research into any of the above
Ordnance Works	sorting production mix-ups	College & University	development and study of new alloys
Other Manufacturers	certification of analysis for finished material	State & Federal Government	temperature measurements of plasma in jets, shock tubes, etc.
	control of plating solutions		uranium isotope analysis
	service failure investigation		
	analysis of ceramics		
<i>Chemical and Petroleum Industry</i>	impurities in catalysts		
	monitoring minor elements and additives		
	impurities in plastic		
	trace elements in CP chemicals		
	corrosion studies		
	geological investigations		

the scale is automatically spread out to give better absolute reading precision.

For the reason discussed above an electronic measuring system was developed to give a logarithmic presentation of data. As already described, the light is converted to electricity and accumulated as a charge on a capacitor during the exposure. After the exposure has been completed, the internal standard capacitor (C_s) is discharged through a resistor (R). Because of the nature of the exponential decline of this voltage, the time involved in falling from the initial voltage (E_s) to one of the unknown element voltages (E_x) will be proportional to the logarithm of the voltage ratio, which in turn is related to the per cent concentration.

Each channel of the readout system consists of a triggering circuit and a timer (either a clock indicator dial or a strip chart recorder). The triggering circuits are simply START-STOP circuits, which start the timers at the start of the readout cycle and stop the timers when the standard voltage falls to the unknown element voltage. By running samples of known analysis a calibration curve can be established relating time or indicator readings to per cent concentration.

Emission Spectroscopy Compared to Chemistry. Emission spectrochemical instruments can eliminate much routine chemical analysis. The accuracy is considerably better than wet chemical methods for trace and minor elements (for example, down to parts per million). For major elements—say 10 % to 40 %—the coefficient of variation of analysis is commonly 3 %–5 % with spectrographs and 1 %–2 % by direct reading spectrometers (for example, chromium in stainless steel by direct reading at 20 % can be determined to within ± 0.15 %). Moreover, many determinations difficult or impossible by wet chemistry are easy by emission spectroscopy—aluminum and boron in steel; cerium and magnesium in iron; trace ele-

ments in lubricating oil and other materials; etc. The users and uses of emission spectrochemical instruments (Table 2) are an eloquent indication of the role played by these techniques.

G. L. CLARK

MOLYBDENUM ANALYSIS

The spectrochemical determination of trace elements in molybdenum is inherently difficult due to the complexity of the molybdenum spectrum and the intense continuum emitted under ordinary d.c. arc excitation.

A technique in which these difficulties are largely avoided involves the following principles: (1) The molybdenum, if not in the metal form, is converted to the metal powder and mixed with pure graphite powder containing the internal standard. (2) The sample mixture is packed into electrode craters, approximately $\frac{1}{8}$ " deep and $\frac{1}{8}$ " in diameter, and arced using high voltage alternating current. (3) A small analytical gap and a relatively short exposure time are used.

Under these conditions, the molybdenum spectrum and background are depressed to the extent that interference from background, halation, and even weak spectral lines is greatly reduced. Formation of the extremely refractory molybdenum carbide during arcing probably accounts for this marked depression of molybdenum. X-ray diffraction patterns of sample residues exhibit strong diffraction lines attributable to molybdenum carbide. In effect, all those impurities which are more volatile than the molybdenum carbide volatilize out selectively before an intense molybdenum spectrum appears.

The sensitivities of many impurities are greatly enhanced as a result of this phenomenon; however, there are impurities that are similar in behavior to molybdenum and their spectra are therefore depressed by this technique. Tungsten is an example of such an impurity. A method whereby good sensitivity can be attained for tungsten is to di-

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TABLE 1. LINE PAIRS AND ANALYTICAL RANGES

	Element	Wavelength, Å	Internal Standard, Å	Range, %
Group	Cr	2677.2	Co 2685.3	0.0006-0.05
	Fe	2483.3	Co 2685.3	0.0005-0.05
	Mn	2576.1	Co 2685.3	0.0001-0.01
	Ni	3002.5	Co 2685.3	0.0006-0.04
	Pb	2833.1	Co 2685.3	0.0009-0.05
	Si	2514.3	Co 2685.3	0.0005-0.05
	Sn	2840.0	Co 2685.3	0.0008-0.05
Group II	Al	3944.0	Ni 3080.8	0.0005-0.05
	Ca	3933.7	Ni 3080.8	0.0001-0.005
	Cu	3274.0	Ni 3080.8	0.0001-0.01
	Mg	2795.5	Ni 3080.8	0.0001-0.02
Group III	Ba	4554.0	Co 7085.0	0.0004-0.003
	Ba	6141.7	Co 7085.0	0.003 -0.01
	K	7664.9	Co 7085.0	0.001 -0.02
	Na	5889.9	Co 7085.0	0.0004-0.01
	Sr	4607.3	Co 7085.0	0.001 -0.01
Group IV	W	4008.7	Mo 4006.0	0.01 -0.2
	W	4102.7	Mo 4006.0	0.2 -1.0

lute the molybdenum metal powder with zinc oxide buffer and excite with low amperage direct current.

A secondary matrix line is suitable for internal standardization in the case of tungsten; however, the more volatile elements require the addition of an internal standard. High purity, finely powdered nickel and cobalt mixed with the graphite buffer are satisfactory internal standards.

Standards. Synthetic standards can be prepared by adding volumetrically standardized solutions of the impurity elements to specially purified molybdenum metal powder. Great care is required not to contaminate during these additions. After drying and blending the standards, it is recommended that a final hydrogen reduction be carried out (except for those standards which contain volatile elements such as Sn and Pb), so that the physical characteristics of synthetic standards approximate unknown samples.

Sample Preparation. The following ratios of sample to buffer give good results:

Group 1 elements (see table)—1.0 gram molybdenum metal powder to 0.28 gram buffer (25 parts graphite: 1 part finely powdered cobalt).

Group 2 elements—1.0 gram molybdenum powder to 0.28 gram buffer (27 parts graphite: 1 part finely powdered nickel).

Group 3 elements—Same mixture as for group 1.

Group 4 (tungsten)—1 part molybdenum metal powder to 1 part zinc oxide by volume.

Table 1 gives suitable line pairs and analytical ranges for a series of common impurities in molybdenum. These elements are grouped roughly in accordance with their spectrochemical behavior.

Molybdenum Trioxide

In essence the above principles are applicable to the analysis of molybdenum trioxide. However, the sensitivities of most of the elements are less favorable. The trioxide is quite volatile and, although carbide formation occurs during arcing, there is an extremely high concentration of molybdenum vapor in the arc column for a few seconds after the arc has been initiated. For this reason a short preburn is recommended. Also a much higher ratio of graphite to molybdenum is required for effective suppression of the molybdenum spectrum.

RUDOLPH DYCK

NONMETALLIC ELEMENTS

Nonmetallic elements present in chemical compounds, usually as a constituent of the negative radical or anion, can be analyzed by optical emission spectroscopy. However, these elements are not excited by conventional spectrochemical methods and other preparations are necessary before identification and evaluation from their emitted spectra are possible. Elements considered to be nonmetallic from the standpoint of spec-

TABLE 1. THE PRINCIPAL SPECTRAL LINE OF SOME OF THE NONMETALLIC ELEMENTS, AS WELL AS THE EXCITATION POTENTIAL (E.P.) OF THIS LINE AND THE IONIZATION POTENTIALS (I.P.) FOR THE ELEMENTS.

Atomic Number	Element	Principal Line A	E.P. (Volts)	I.P. (Volts)
6	C	1656.994	7.45	11.22
9	F	954.817	12.92	18.6
15	P	1774.942	6.95	11.1
16	S	1807.37	6.83	10.3
17	Cl	1347.2	9.16	12.96
34	Se	1960.87	6.29	9.5
35	Br	1488.40	8.29	11.80

troscopy and which are commonly encountered are carbon, sulfur, selenium, phosphorus, fluorine, chlorine, bromine, iodine, and gaseous elements such as hydrogen, oxygen, and nitrogen.

The characteristic spectral lines of non-metallic elements have excitation potentials some 2 to 4 times greater than those of the metallic elements with potentials of the order of 4 to 8 electron volts. In an electrical discharge the effective energy potential is largely dominated by the elements with low excitations and elements with high potentials are suppressed. Thus, in a compound consisting of both cations and anions the potentials necessary to excite spectral lines of non-metallic elements are not normally reached. The principal spectral line of some of the nonmetallic elements, as well as the excitation potential of this line and the ionization potentials for the elements are listed in Table 1.

Many spectrochemical methods for the analysis of nonmetallic elements have been suggested in literature. An important consideration of all methods is the selection of proper excitation conditions sufficient to obtain emission spectral lines or bands in an accessible analytical region of the spectrum. Sparks with high average excitation, powerful low-tension sparks, arcs with high-current density, hollow cathode excitation, and

high-frequency excitation at low pressures have all been used successfully. Spectrographs operated in a vacuum or an inert atmosphere permit the use of sensitive spectral lines below 2000 Å. Some halogens, mainly fluorine, and carbon can be analyzed by band structures emitted from molecular combinations, such as CaF or CN, which are formed in an arc column.

Spectrochemical methods are advantageous over other analytical methods under a number of conditions. However, established chemical methods are very often more direct, cheaper, and more accurate when only a few samples are to be analyzed for several elements at high concentration levels. When only small amounts of sample material are available or when trace impurities are to be detected, spectrochemical methods are usually the best approach for analyses. Spectrochemical methods are especially adaptable to control systems whereby samples are to be run on a continuous basis. The results improve in accuracy and ease of determination as the analyst gains in experience. Spectroscopy has the added advantage in that a number of elements, cations, and anions can be determined simultaneously. Ideally, all elements present in a sample could be analyzed by a single method. However, this not being the case, a number of methods are necessary before all analytical conditions can be met. The method chosen for a given analysis is based on the elements to be determined, their concentration level, the amount and state—whether solid, liquid, or gas—of the sample material, and the analytical equipment available to the analyst.

Direct-Current Arc

Fluorine and Other Halogens. Fluorine and other halogens are analyzed in a direct-current arc by the use of band structures from diatomic molecular emitters formed in the arc column by the combination of the halogen with an alkaline earth. The

CaF emitter is found to be the most stable in an arc of any of these combinations with the result that fluorine has the lowest detection limit of the halogens— ~ 50 ppm. Procedures for detection of fluorine in water, rocks, minerals, slags, and enamels are reported in literature.¹⁻¹¹ Other combinations of a halogen and an alkaline earth are relatively unstable and are not as extensively used as the CaF emitter.

CaF bands are easily excited, $\sim 2\text{--}3\text{ eV}$ excitation potential, and are almost as easily dissociated at ~ 3.3 eV. Thus, emission in an arc is at a maximum at the cooler fringe and at a minimum in the hotter core of the discharge. Bandheads for CaF and other diatomic emitters are given in Pearse and Gaydon.¹² The most satisfactory CaF bandhead for spectrochemical analysis is located at 5291.0 Å. The strongest is 6036.9 Å which can be used for detection of low concentration, but not normally for densitometry because of interference from calcium oxide bands.

An excess of calcium atoms in the arc column is necessary for the formation of CaF emitters, and if calcium is not present in the original sample material it can be added as any one of its compounds. The most common practice is to add both calcium as CaCO_3 and carbon powder to the sample material to ensure both a copious release of calcium atoms during the early period of arcing and at the same time minimize selective volatilization. Fluorine is very volatile while calcium is much less so and any factor which accentuates this difference in volatility tends to decrease detection sensitivity.

The intensity of CaF band emission is fairly sensitive to matrix changes and standards should be selected with this in mind. Several certified standards with different matrices are available from the National Bureau of Standards and can be used as a starting material for making a series of synthetic standards for working curves. One NBS standard, No 91, is an opal glass with

$\sim 5.7\%$ F and two others, Nos. 56 and 120, are phosphate rocks with $\sim 3.7\%$ F.

Optimum conditions for fluorine analysis vary somewhat for different sample materials. No one set of conditions is the best for all materials. However, there are some conditions which apply to all analyses. Satisfactory results for fluorine in phosphate rocks are obtained with a mixture of one part sample and two parts of a 1:1 mixture of CaCO_3 and carbon powder. A portion of the sample mix is excited in a $\frac{3}{16}$ " carbon anode for 30 seconds at 7 amperes. The optimum excitation time for other materials varies according to percentage fluorine, sample volatility, CaCO_3 to carbon powder ratio, electrode design, and arc current used. Since the analytical bandheads are located in the visible region, a photographic emulsion with maximum sensitivity to that region is necessary. Eastman III-J or I-L emulsions are adequate for most analyses. A spectrograph with a dispersion of 8 Å/mm or better is desirable. Transmittance values of the 5291.0 Å bandhead, corrected for background, are plotted against fluorine concentration values of standard samples to obtain analytical working curves. Several curves are needed to cover the analytical range between several tenths of a per cent to 6% or greater. Duplicate determinations are usually necessary. Reproducibility for fluorine analysis are about $\pm 15\text{--}20\%$. Some improvement can be gained by the use of an internal standard, such as the CaO bandhead at 5488¹ or a copper line at 5105.5 Å,⁵ but very often the gain does not warrant the added effort. Detection limits are obtained down to 100–200 ppm. The detection limit for fluorine can be extended to 40–50 ppm by arc excitation in a helium atmosphere.¹ CaO bands are, thereby, suppressed and the more sensitive CaF bandhead at 6036.9 Å can now be used. Usually three superimposed exposures of 60 seconds are needed for the lowest detectable concentrations.

Fluorine determinations in calcined alu-

mina and other materials can be applied to direct-reading spectrochemical instrumentation.¹³ Both CaF and SrF band structures are satisfactory for concentration values of 0.05 to 0.5% in air and 0.02 to 0.3% in a helium atmosphere.

The SrF bandhead at 5772 Å can be used for fluorine detection similarly to the CaF bandhead at 5291 Å with about the same level of detection. However, CaF 5291 Å is preferred for most analysis because calcium is more prevalent than strontium in most sample materials. When both calcium and strontium atoms are present in the same arc column the available fluorine is distributed between the two emitters with a resultant decrease in sensitivity. BaF bandheads are observed in the arc but are found to be not as clearly defined or as sensitive as the CaF and SrF bandheads.⁸

Chlorine combined with calcium emits in an arc several bandheads suitable for spectrochemical analysis of which 5934.0 and 6211.6 Å are found to be the strongest.⁸ Methods for analysis are similar to fluorine detection. Chlorine also combines with barium to form bandheads, however, the strongest, 5240.5 and 5136.0 Å, are less sensitive than the CaCl bandheads.

Bromine combines with barium to form weak emitters with bandheads at 5208.2 and 5360.1 Å. Thus far, iodine detection by band structures has not been reported in literature.

Halogens also combine with elements other than the alkaline earths to form emitters of molecular spectra. Pearse and Gaydon¹² gives the identification of a number of halogen diatomic molecules that are excited in the arc which possibly can be used for the detection of halogens. However, most combinations are easily dissociated and are best suited to the conditions of the low excitation potentials which exist in flames.

The alternating-current arc has also been used for the analysis of fluorine by the CaF bands.¹⁴

Carbon. Carbon is analyzed in its various compounds by use of the direct-current arc.¹⁵ When samples are excited in copper electrodes, the carbon in the sample combines with atmospheric nitrogen to form cyanogen which emits bandheads that are used as a measure of the amount of carbon present. The cyanogen violet system, with principal bandheads at 3590, 3883 and 4216 Å is the most sensitive of the various cyanogen systems with the bandhead at 3883 Å being the most sensitive and used for spectrochemical analysis. The excitation potential for the cyanogen violet system is ~3.2 eV as compared with 3.77 eV for copper which ensures cyanogen excitation in a copper arc. The intensity of the cyanogen bands increases with higher amperages with cathode excitation, however currents in excess of 6 A are not used because the copper electrodes will melt.

The complex process whereby cyanogen is formed and excited in the arc is subject to many variables which affect the relative intensity of the cyanogen bands produced from a given amount of carbon in the sample material. The principal variables to be considered are the widely different carbon-bond strengths, the effect of excitation changes, and the control of arc temperatures by extraneous elements. These factors will all affect the rate and completeness of evolution of carbon or carbon containing compounds from the sample.

Time studies of volatilization show that cyanogen production occurs very early in the arcing period for most samples, presumably through rapid evolution of the carbon as CO₂. The presence of alkalis or other easily excited elements in the sample material tends to lower the arc temperature and, thereby, suppresses the formation of the cyanogen bands. However, the presence of silica greatly enhances the relative intensity of CN 3883 Å because the decomposition of carbonates is accelerated by chemical reaction in the hot electrode of the silica with the carbonates.

The addition of one part of quartz (SiO_2) by volume to all samples and standards reduces this matrix effect and simplifies standardization.

Carbon can be determined spectrochemically either as carbonate carbon or as "equivalent graphite" carbon or as both forms in the same sample. Two series of standards, which can be made from available National Bureau of Standards materials, are needed to cover both forms. Standards for "equivalent graphite" carbon, or graphitic carbon, can be made by mixing pure carbon powder with pure quartz or a NBS glass sand—Nos. 81 or 165. The carbonate carbon, calculated as percentage CO_2 , can be NBS Nos. 1a and 88 used directly, or chemically analyzed standards, or even quartz mixed with known quantities of CaCO_3 . Both samples and standards are ground to pass a 100 mesh screen and diluted with one part by volume of quartz before arcing.

Electrodes are cut from commercial copper rods of 3 mm diameter, and a cone-shaped cavity with an apex angle of 82° is machined in one end. The sample mix is packed into this cavity, but not weighed. Counterelectrodes are cut from commercial copper rods of 1.5 mm diameter.

The sample electrodes along with appropriate standards are excited in the direct-current arc for 30 seconds and 6 A at ~ 50 V. The sample electrode is the cathode. Spectrographs with an 8 Å/mm dispersion or better are satisfactory for all analysis. The resultant spectra are recorded on a photographic emulsion sensitive to the 3000–4000 Å region. The CN 3882 Å bandheads, corrected for background, are measured and transmittance values obtained are converted to log relative intensities by means of the emulsion calibration curve. The percentage carbon present in a sample is determined from analytical working curves of log relative intensity CN 3883 Å versus log per cent carbon or CO_2 values of standard samples. Since differences in the matrix do not change the slope of the ana-

lytical curves for graphitic carbon or for carbon in the carbonates, the same curve but with different abscissas can be used for both. The analytical range for graphitic carbon is from about 0.1 to 50.%, and for CO_2 from about 0.5 to 50.%. The precision of low-carbon contents is somewhat decreased by small amounts of CO_2 in the atmosphere and by CO_2 absorbed in the electrodes, the sample itself, and the quartz diluent. Some correction for this CO_2 can be made by arcing a bland quartz sample. The coefficient of variation of this method as determined by replicate determinations is found to be 13%.¹⁵

If carbon is to be determined as carbonate carbon and as graphitic carbon in the same sample, the sample is divided into two parts. One part receives no further treatment other than the addition of one part quartz, while the other part is treated with warm 1N HCl to eliminate CO_2 . The solution is filtered and the residue is dried, weighed, and quartz added. Arcing untreated samples provides a CN 3883 Å intensity representing the total carbon content, while arcing the residue from HCl treatment gives that portion of the total intensity which is attributed to "equivalent graphite," provided appropriate corrections are made. The difference between the untreated sample and the residue is then due to carbon evolved as CO_2 .

The analytical range for carbon determinations from the cyanogen bandheads can be extended down to $\sim 0.01\%$ by sparking in a nitrogen atmosphere at a reduced pressure of 10–20 mm of Hg.¹⁶ In this case, the sample material is mixed in a 1:1 ratio by volume with silver powder and briquetted. The pellet is then sparked with a silver counter-electrode in an atmospheric control chamber. The N_2^+ bandhead at 3914 Å is used as an internal standard for the CN 3883 Å bandhead.

Selenium. The most persistent arc line of selenium, 1960.9 Å, is not satisfactory for spectrochemical analysis unless the optical

path is a vacuum or an inert gas. The line is partially absorbed by the quartz in the optical system, by the oxygen in the air, and by the gelatin in the photographic emulsion. However, the second most sensitive lines, 2039.9 and 2062.8 Å, are in a slightly more favorable region and can be used with certain considerations to detect selenium down to 0.001% without previous chemical concentration of the selenium.¹⁷ The excitation potential of the second selenium line pair, 6.3 eV, is lower than the carbon, 7.7 eV, of the electrode material but higher than most elements present in the sample materials. Other suggested methods for arc excitation¹⁸⁻¹⁹ require some method of chemical concentration of the selenium before analysis.

Short wave length radiation emulsions manufactured by Eastman, and Ifford Q emulsions make possible the recording of the selenium line pair at 2039.9 and 2062.8 Å. Also, experimentation has shown that this line pair is greatly enhanced by the addition of copper oxide to the sample matrix. The copper oxide also ensures an even burn in the arc. The combination of the sensitive emulsion and the copper oxide buffer permits the analysis of selenium in the range of 2 to 0.001%.

Sample materials can be thoroughly mixed by passing through a 100 mesh screen for ~30 times. If the history of the sample is unknown, a preliminary test using 40 mg of the sample is necessary to set the Se concentration above or below the 0.01 to 0.1% range. If the concentration is below 0.01 an 80 mg sample is used and if above 0.1 a lesser amount is used. Table 2 shows the correct sample weights. In application of this method, 40 mg of copper oxide is added, regardless of the sample weight. Analytical standards can be made by the addition of known quantities of selenium to the proper sample matrix, or by a chemical determination of the selenium content.

The samples along with appropriate

TABLE 2. SAMPLE WEIGHTS FOR DIFFERENT SELENIUM PERCENTAGES

Mg of Sample	Range % Selenium
10	1-10.
20	0.1-1.
40	0.01-0.1
80	0.001-0.01

standards are placed in the craters of $\frac{1}{4}$ " graphite electrodes and excited in the direct-current arc at 12 A and 300 V for 90 seconds. The resultant spectra are recorded on a short wave length radiation emulsion. The 2039.9 Å selenium line is measured and the percentage present is determined from analytical working curves made from a plot of known per cent selenium versus blackening of the 2039.9 Å line.

A check of this method with chemically analyzed samples shows a relative accuracy of about 7% of the amount present. Although this spectrochemical method has been applied only to several minerals—pyrite, chalcocite, and marcasite—it is believed that satisfactory results can be obtained with many other sample materials.

Spark Excitations

Several different spark conditions have been suggested which are sufficient to produce the emission spectra of nonmetallic elements in a spectral region convenient to most spectrographs. Usually more than one spectral line of each element is excited and is available for spectrochemical analysis. The concentration range from parts per million to the major constituent can be covered. Although satisfactory results are obtained by sparking in air, limits of detection are extended and reproducibility of results are improved by sparking in a controlled atmosphere at reduced pressures.

Commercially purchased source units can be used for excitation. One of these is the Applied Research Laboratories standard spark unit. The most "sparklike" condition

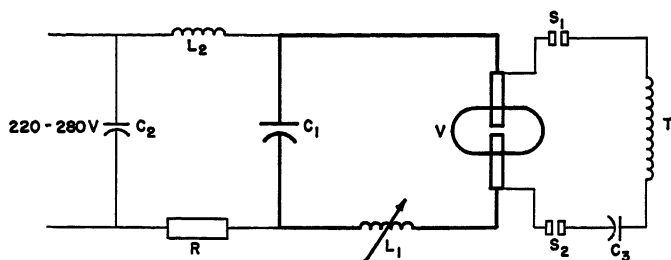


FIG. 1. The Pfeilsticker low-tension spark circuit for excitation of nonmetallic elements. Incoming voltage 220–280 V a.c., C_1 400–2000 μ F, C_2 0.1 μ F 1500 V, C_3 0.25 μ F 350 V, L_1 0–5 μ H, L_2 line-filter inductance, R load resistance 10–40 ohms, V vacuum chamber—pressure 2 to 20 mm Hg, T Tesla coil.

for this unit is 0.021 μ F capacitance and 45 μ H inductance which is sufficient for excitation of most nonmetallic elements.²⁰ The ARL Model 4700 high precision source unit operated with its most highly condensed sparklike discharge is also satisfactory.²¹ In this case, the air inductance coils are removed from the circuit so that a minimum of residual inductance remains. For sample excitation, a nominal radio-frequency current of 8 A is passed through a 0.5 mm analytical gap for a 30 second period. Another source is the air interrupted spark with 0.015 μ F capacity charged to 14,000 peak volts and discharged 3 times per half-cycle through a resistance of 2 ohms, an inductance of 50 μ H, and an analytical gap of 0.5 mm.²² For a high-voltage spark source with a synchronous interrupter, a condenser of 0.02 μ F capacity is charged to 34,000 peak volts and discharged through a 8.8 ohms resistance, an inductance of 50 μ H, and an analytical gap of 0.5 mm.²² The resultant *rf* current for these conditions is 14 A.

A powerful low-tension spark circuit developed by Pfeilsticker,^{23–24} Figure 1, has proved to be very effective in the excitation of nonmetallic elements. Characteristics of this circuit are discussed in literature.^{25–28} Experimentations have shown that as the duration period is shortened and the current density is increased, the characteristics of an arc discharge become more sparklike as revealed by the increase in number and intensity of spark spectral lines. Sparklike

spectra are obtained when condensers of 400 to 2000 μ F at 300 V are discharged through a resistance between 10 and 40 ohms, an inductance of 0–5 μ H in a duration period between 0.01 and 0.5 seconds. Currents up to 10,000 A have been reported for this discharge.²⁸

One method for sample preparation for excitation is to mix a few milligrams of powdered sample material with an equal volume of fine mesh silver powder and to press the mix into a pellet, either with a mechanically or hand operated press. The size of the pellet can be from an $\frac{1}{8}$ " to a $\frac{1}{4}$ " diameter. The bulk of the pellet can be increased by adding silver powder or a solid silver rod between two portions of sample mix and then pressing into a pellet. In this way, besides increasing the bulk of the pellet, duplicate results are obtained by sparking both ends of the pellet. The counter-electrode can be either pelleted silver powder or a solid silver rod. An internal silver standard, if desired, is introduced by mixing into the silver powder. Powered zinc²² and bromine, introduced as a compound,²¹ have been suggested as internal standards.

Spark discharges usually produce spectra having more than one line of each nonmetallic element present, thus a broad analytical range can be covered in a single exposure. Analytical lines in the spectral region between 3500 and 5000 Å are shown in Table 3.

Standards are prepared either by chemical analysis or by the addition of known quantities of the elements to be determined to the

TABLE 3. USEFUL SPECTRAL LINES OF NONMETALLIC ELEMENTS FOR SPARK ANALYSIS IN THE 3500-5000 Å REGION

C	F	P	S	Cl	Se	Br	I
3876.2	3503.1	3556.5	3497.3	3602.1	3637.5	3506.5	3498.0
3876.4	3505.6	3706.1	4142.3	3748.3	3711.6	3517.4	3724.8
3876.7	3847.1*	3827.4	4145.1	4794.5*	3738.7*	3540.1	3897.3
3920.7	3850.0	4475.3	4153.1	4810.1*	3800.9	3562.4	
4074.5	4024.7	4587.9*	4162.7*	4819.5*	4382.9	4704.9*	4409.0
4076.0		4601.2*	4174.3	4896.8		4785.5*	4452.9*
4267.0			4525.0	4904.8		4816.7*	4512.6
4267.3*							4666.5

* Strongest lines

appropriate sample matrix and mixing into the powdered silver used for the formation of the pellet. Standards are treated to the same analytical conditions as the unknown materials.

Analytical curves for sulfur between 1 and 18 %, and chlorine between 1 and 45 % can be established from spectra produced under ordinary atmospheric conditions within an average deviation of 18 %.²¹ By blowing an inert gas through the spark discharge zone, background is suppressed and spectral line intensities are enhanced.²² To further extend detection limits down to 1 μ g or less necessitates the use of an atmospheric control chamber with an inert gas at pressures of 2 to 20 mm of Hg. The powerful low tension spark requires a specially designed chamber.²³⁻²⁴ Another design that can be used with most other spark discharges¹⁶ is shown in Figure 2.

Carbon in Steel. Carbon is determined in steels by excitation with a condensed spark. The sample is one electrode and the counter-electrode is either silver, copper, or magnesium, or another conductor. Metallographic conditions of the sample must be considered in the selection of standards. The carbon line CIII 2296.9 Å used with the iron line FeIII 2295.9 Å as an internal standard can give results within a coefficient of variation of about 3.7 % of the carbon content.²⁹ With low carbon steels the CO₂ present in the atmosphere can interfere unless proper

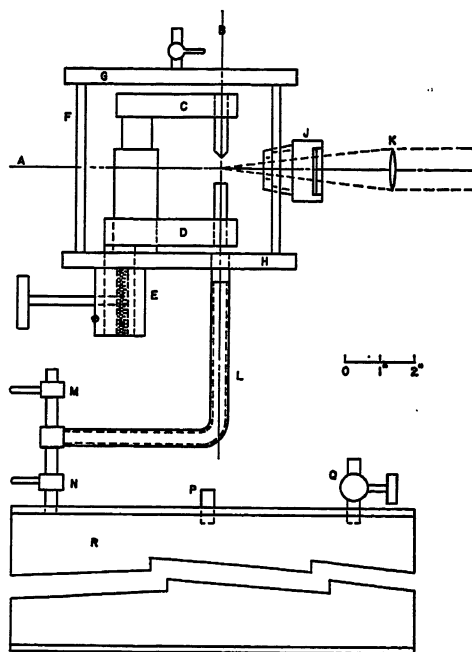


FIG. 2. An atmospheric control chamber for spark excitation of nonmetallic elements. (Courtesy C. E. Harvey Assoc., Chicago, Ill.) A. Optical center line; B. Electrode center line; C. Upper electrode holder; D. Lower electrode holder; E. Lower electrode adjuster; F. Plexiglas vacuum chamber; G.-H. Vacuum closure plates; J. Quartz window insert; K. Condensing lens; L. Vacuum or pressure line; M. Valve to inert gas; N. Valve to vacuum reserve tank; P. Manometer connection; Q. Valve to vacuum pump; R. Vacuum reserve tank.

steps are taken to eliminate or minimize the effect. The use of a magnesium counter-electrode prevents the formation of a thick oxide

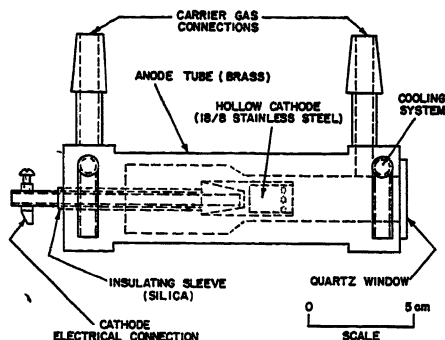


Fig. 3. A schematic drawing of a hollow cathode for analysis of nonmetallic elements. (After Birks²⁷)

film on the sample electrode, lowers the rate of carbon oxidation, and reduces the diffusion rate of the CO_2 into the surrounding gaseous medium.³⁰ Thus, the carbon spectral line is enhanced and analytical results are obtained down to 0.03–0.04 %.

Hollow Cathode

Hollow cathode excitation is the most sensitive of any spectrochemical method for the detection of most nonmetallic elements. Also, the sample form can be either a solid, a liquid, or a gas. However, the design and operation of the hollow cathode are complex, and to obtain results for routine analysis requires ingenuity as well as experience. The method is very sensitive because the discharge is almost completely confined to the inside of the cathode, little material is lost from the discharge, the efficiency of excitation is high, and the sample material is repeatedly re-evaporated into the discharge.³¹ The source is especially suited for the analysis of materials available only in minute quantities. The hollow cathode was originated by Paschen³² and further developed by Schüller^{33–34} and by others^{35–39}.

If the cathode is made hollow and a d.c. potential of about 1000 V is applied in a pressure from 1 to 10 mm of Hg a brilliant glow is produced which is concentrated within the cathode space. The glow is characterized by low potential gradients and an

almost pure electron excitation. The electron velocities are limited by the critical potentials of the carrier gas. The intense positive ion stream of the carrier gas causes sputtering of the cathode or any material lining it, the particles of which are then excited by collisions of the second kind with positive ions. The excitation potential of helium, commonly used as the carrier gas, is 19.7 eV and this is sufficient for the excitation of the spark spectrum of most nonmetallic elements, and in particular the halogens. Mixtures of several gases, such as helium and argon, can also be used to combine sputtering effectiveness along with high excitation conditions.

A simplified design of a hollow cathode is shown in Figure 3. The cathode is made by drilling a concavity in the end of a rod of any one of a number of materials such as stainless steel, tungsten, or graphite. The anode, which forms the outer envelope of the system, can be constructed from brass. The anode, insulated from the cathode, is cooled by a water circulation system or by immersion in liquid air to permit higher currents and to give maximum line sharpness. The carrier gas is a source of contamination and must be thoroughly purified before entry into the system. This can be accomplished by continuous circulation of the gas through a liquid-air cooled charcoal trap. A quartz window is sealed at the end toward the spectrographic slit.

Sample weights of 20 mg or more are introduced into the system by coating the material as a fine powder onto the hollow of the cathode. Sample weights of more than 100 mg are undesirable since distortion of the discharge will occur and sputtering of impurities will be incomplete. The sample can also be added in solution form by evaporating the solution to a thin uniform film within the cathode. The system is outgassed and the purified carrier gas is added to a pressure between 1 and 10 mm Hg. A satisfactory power source is a smooth direct-current sup-

ply with an available voltage up to 1500. The anode is grounded. Exposure times of five minutes at 0.3 A or six minutes at 0.2 A are needed to remove all the halogens and the sulfur from the sample. A photographic emulsion with high sensitivity from 4000 to 9000 Å, such as Eastman I-F or I-N emulsions, is necessary to record spectral lines in the correct analytical region. Table 4 lists some spectral lines of the halogens along with sensitivities found in helium.³⁷ The standard deviation for the determination of fluorine was found to be 12.4%.³⁷ The use of a helium line as an internal standard improved the results only to 11.3%.

Hollow cathode analysis is limited to materials, or ones containing constituents, which can be volatilized by the positive ion stream. The temperature at the cathode rises with an increase in current and cannot exceed the boiling point of the cathode material. By using a graphite cathode with a 2 A current, a temperature of 2500°C at the sample material has been obtained.³⁹

Hollow cathodes are so constructed that they may be disassembled, cleaned, and repeatedly reused.

High-Frequency Excitation

The halogens, selenium, and sulfur can be analyzed from their spectra excited by a high-frequency field in a high-vacuum system.⁴⁰⁻⁴¹ The excitation chamber consists of a quartz, or a high-melting point glass tube with a ground joint connection for sample loading at one end and a quartz-window optic at the other. High-frequency coils are wound around that portion of the tube containing the sample. The tube is evacuated to a pressure of 10^{-3} mm Hg or less, and a high-frequency field is applied to the coils. Short-wave transmitters in about the 6 meter range, or other high-frequency generators with a power rating of 300 watts are sufficient for most excitations.

When solid sample materials are analyzed, a sufficient vapor pressure must be obtained

TABLE 4. SPECTRAL LINES OF THE HALOGENS USED FOR HOLLOW CATHODE ANALYSIS

	Spectral Line Å	Geissler Intensity	Sensitivity in Helium, Micrograms
F	6856.0	1000	0.5
	6902.4	500	0.8
	7128.0	150	0.1
	7202.4	125	0.25
	7398.7	400	1.
Cl	4794.5	350	1.
	4810.1	200	1.
Br	4785.5	400	7.
	4816.7	300	10.
	8272.4	70	5.
I	4808.0	15	2.5
	4986.9	35	2.5
	5678.1	80	2.5

for excitation. Excitation depends on the volatilization of the sample, or constituents of the sample, into the discharge area. The low thermal power of this electrodeless discharge limits the application of the method to materials with low vapor pressures. A temperature of 1100°C can be reached. Higher temperatures will cause the walls of evacuated tubes to collapse. Sample weights of 10 to 20 mg are normally used. Analytical spectral lines for the halogens are about the same as those used in spark excitations (Table 3). The sensitive selenium lines at 2039.9, 2062.8, and 2074.8 can be used. Other selenium lines as well as the sulfur lines appear in the 4500–5500 Å region. Under favorable conditions, sensitivity limits of 0.001% are obtained. Quantitative results are made down to 0.01% with an accuracy of 10%.

Vacuum Ultraviolet Region

The nonmetallic elements have sensitive spectral lines which are useful for analysis and are relatively free from interference that appears in the region having wavelengths shorter than 2000 Å.⁴² The high absorption of the atmosphere in this region makes it

EMISSION SPECTROSCOPY—LIGHT

TABLE 5. THE CONCENTRATION RANGES AND THE COEFFICIENT OF VARIATION OF RESULTS FOR CARBON, PHOSPHORUS, AND SULFUR IN STEELS BY VACUUM SPECTROMETRY.

	Spectral Line A	Concentration Range %	Coefficient of Variation
Carbon	1930.9	0.003 to 2.25	1.2
Phosphorus	1774.9	0.001 to 0.15	1.1
Sulfur	1807.3	0.001 to 0.10	2.6

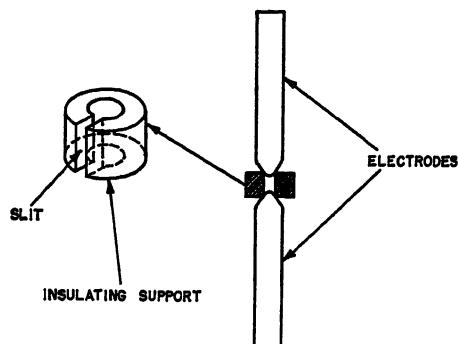


FIG. 4. Electrode configuration for the "sliding spark."

TABLE 6. THE MOST SENSITIVE LINE OF SOME OF THE NONMETALLIC ELEMENTS IN THE FAR ULTRAVIOLET REGION.

	A		A
C IV	1548.19	Se VI	844.15
P V	1117.98	Cl VII	800.70
S VI	933.38		

essential to work with spectroscopic equipment that has been evacuated or that has been filled with a transparent gas such as hydrogen or helium. With the advent of commercially made vacuum spectrographs with optics of calcium or lithium fluoride and with aluminized diffraction gratings, operation in the vacuum ultraviolet is facilitated and becomes practical for many analytical problems. Vacuum spectroscopic equipment is available from several American manufacturers, namely, Applied Research Laboratories, Jarrel-Ash Co., and Paul M. McPherson.

Spark and "sparklike" conditions, such as the ones suggested previously, will produce excitation in the vacuum ultraviolet region. The hollow cathode as well as high-frequency excitation can also be used. Although the most sensitive arc lines of the nonmetallic elements are located in this region, they are not normally used for detection of low quantities because conditions for excitation in a vacuum or an inert gas favor the emission of spark lines.

Steels are analyzed by automation for carbon, phosphorus, and sulfur as well as other constituents by vacuum spectroscopy.⁴³⁻⁴⁴ Detection limits are thereby extended and reproducibility of results is improved. In some cases, the sample is sparked using a silver counter electrode in an excitation chamber filled with argon. A window and lens made of either calcium or lithium fluoride separate the chamber from the main body of the spectrometer which is evacuated from the entrance slit to the multiplier phototube windows. Individual phototubes are set for each analytical line and the internal standard line. Results are received on a console used for integrating and recording electrical impulses. Some analytical lines along with their concentration ranges and coefficient of variation of results are given in Table 5.

Very high excitation energies are used to obtain the spectra from nonmetallic elements that have been highly ionized with but one or two electrons remaining in the outer shell. The emitted lines from most highly ionized nonmetallic elements are in the spectral region between 800 and 1200 Å. A method of excitation, called the "sliding spark",⁴⁵ is produced *in vacuo* between electrodes in contact with an insulating or semi-conducting support. The support has a narrow opening in the direction of the spectrographic slit as shown in Figure 4. An example of the power needed to produce the ionized spectra is an electrical circuit with parameters of 0.75 μ f,

14 μ h, 25 kV at a discharge rate of 20 to 30 per minute.

The spectroscopic system, including the excitation unit, is evacuated to around 10^{-4} mm of Hg. Ten to 100 discharges are needed for proper intensity of exposure. The emitted spectra are recorded on a photographic emulsion that has been specially sensitized to the far ultraviolet region. The most sensitive lines in the far ultraviolet region for some of the nonmetallic elements along with the degree of ionization are given in Table 6. The detection and analysis of sulfur, phosphorus, and carbon in steel and in aluminum have been investigated. Other analyses have been sulfur in copper and silver, sulfur in fluorite, and chlorine in certain powders. Detection limits are in the 5 to 100 ppm range.

REFERENCES

1. AHRENS, L. H., "Quantitative Spectrochemical Analysis of Silicates," Addison-Wesley, Cambridge, Mass., pp. 93-8, 1955.
2. AHRENS, L. H., "Spectrochemical Analysis," Addison-Wesley, Cambridge, Mass., pp. 145-51, 173-6, 1950.
3. CASTRO, R., AND LOUDE, R., *Spectrochim. Acta*, **4**, 496 (1952).
4. CHURCHILL, H. V., *J. Am. Water Works Assoc.*, **23**, 1399 (1931).
5. GILLIS, J., ECKHOUT, J., AND KEMP, N., *Rev. universelle mines*, **8**, 284 (1952).
6. JAFFE, H. W., *Am. Mineral.*, **34**, 667 (1949).
7. JOHNSON, W. W. A., AND NORMAN, D. P., *Ind. Eng. Chem., (Anal. Ed.)*, **15**, 119 (1943).
8. MONNOT, G. A., *Spectrochim. Acta*, **6**, 153 (1954).
9. PETERSON, M. J., KAUFFMAN, A. J., AND JAFFE, H. W., *Am. Mineral.*, **32**, 322 (1947).
10. SPINDLER, D. C., AND SMITE, M. F., *Anal. Chem.*, **30**, 1330 (1958).
11. WAINER, E., AND DUBOIS, E. M., *Bull. Am. Ceram. Soc.*, **20**, 4 (1941).
12. PEARSE, R. W. B., AND GAYDON, A. G., "Identification of Molecular Spectra," John Wiley and Sons, Inc., New York, 2nd ed., 1950.
13. LEMIEUX, P. E., AND BLACK, R. H., *Pitts. Conf. on Anal. Chem. and Appl. Spec.*, Pitts., Pa., March 2-6, 1959.
14. SMOLIAX, I., *Eng. Trans. of the Bull. of the Acad. of Sc. of the USSR, Columbia Tech. Trans.*, White Plains, N. Y., **19-2**, 199 (1955).
15. DENNEN, W. H., *Spectrochim. Acta*, **9**, 89 (1957).
16. HARVEY, C. E., "Research Investigations of Semiconductor Impurities," Signal Corps Contract No. DA 36-039 SC-78267 (1959).
17. WARING, C. L., WORTHINGTON, H. W., AND HAZEL, K. V., *Anal. Chem.*, **30**, 1504 (1958).
18. FELDMAN, C., *J. Opt. Soc. Am.*, **35**, 180 (1945).
19. ROCKENBAUER, W., AND SCHROLL, E., *Österr. Akad. Wiss., Math.-naturw. Kl.*, **92**, 192 (1955).
20. HARVEY, C. E., AND MELLICHAMP, J. W., *Amer. Assoc. of Spectrographers*, Chicago, Ill., June 9-11, 1958.
21. GUNN, E. L., *Anal. Chem.*, **26**, 1815 (1954).
22. MANSFIELD, W. O., FUHRMEISTER, J. C., AND FREY, D. L., *J. Opt. Soc. Am.*, **41**, 412 (1951).
23. PFELSTICKER, K., *Spectrochim. Acta*, **1**, 424 (1940).
24. PFELSTICKER, K., *Mikrochim. Acta*, 358 (1955).
25. BILLS, K. M., *Coll. Spec. Int. VI*, Amsterdam, Pergamon Press Ltd., London, 282 (1956).
26. LAQUA, K., *Spectrochim. Acta*, **4**, 446 (1952).
27. VAN CALKEER, J., AND LEHMANN, K., *Coll. Spec. Int. VI*, Amsterdam, Pergamon Press, Ltd., London, 280 (1956).
28. VAN CALKEER, J., *Spectrochim. Acta*, **5**, 19 (1952).
29. GARTON, F. W. J., *Spectrochim. Acta*, **3**, 68 (1947).
30. KUDELIA, E. S., AND DEM'IANCHUK, A. S., *Eng. Trans. of the Bull. of the Acad. of Sc. of the USSR, Columbia Tech. Trans.*, White Plains, N. Y., **19-2**, 139 (1955).
31. SAWYER, R. A., "Experimental Spectroscopy," pp. 27-28, Prentice-Hall Inc., New York, 1951.
32. PASCHEN, F., *Ann. d. Physik*, **50**, 901 (1916).
33. SCHÜLER, H., *Physikal. Z.*, **22**, 264 (1921).
34. SCHÜLER, H., *Z. Physik*, **72**, 423 (1931).
35. ARROE, O. H., AND MACK, J. E., *J. Opt. Soc. Am.*, **40**, 386 (1950).
36. BECART, M., DEPPEZ, G., AND ROIG, J., *Coll. Spec. Int. VI*, Amsterdam, Pergamon Press Ltd., London, 342 (1956).
37. BIRKS, F. T., *Spectrochim. Acta*, **6**, 169 (1954).
38. McNALLY, J. R., HARRISON, G. R., AND ROWE, E., *J. Opt. Soc. Am.*, **37**, 93 (1947).
39. ROSEN, B., AND OTTELET, M. I., *Coll. Int. de Spec. de Strasbourg*, Oct. 12-14, (1950).
40. GATTERER, A., *Spectrochim. Acta*, **3**, 214 (1949).
41. SCHROLL, E., AND ROCKENBAUER, W., *Coll. Spec. Int. VI*, Amsterdam, Pergamon Press Ltd., London, 338 (1956).

EMISSION SPECTROSCOPY—LIGHT

42. HARRISON, G. R., LORD, R. C., LOOFBOUROW, J. R., "Practical Spectroscopy," Prentice-Hall, New York, pp. 530-46, 1948.
43. ANDERMANN, G., "Suggested Method for the Complete Spectrochemical Analysis of Carbon and Low Alloy Steels Using a Vacuum Spectrometer," Applied Research Laboratories, Glendale, Calif., 1958.
44. Hilger Journal IV, 19 (1957).
45. ROMAND, J., BALLOFFET, G., AND VODAR, B., Coll. Spec. Int. IV, Amsterdam, Pergamon Press Ltd., London, 268 (1956).

J. W. MELLICHAMP

OPTICAL MASER* (LASER)

Announcement was made in May 1960 of the support by The Royal Society in England of the construction by Dr. J. H. Sanders of Oxford of an optical maser—a light source with a more precisely defined wavelength peak than any other light available to the spectroscopist. When brought to a focus the beam will possess such purity and intensity that it may be possible to study for the first time the interactions of photons, the particles of light, with one another.

The maser originally gets its name from "microwave amplification by stimulated emission of radiation." Ruby crystals are already in service as masers; they can be used as radiofrequency amplifiers at radar wavelengths because energy can be pumped into them for release by the stimulation of the incoming signal. A year ago Professor C. H. Townes and A. L. Schawlow in the United States proposed that this idea of pumping and stimulated emission could be applied to visible light as well as to microwaves. Since then one has seen the first tentative steps taken towards an optical maser, mainly in the United States, where Dr. Sanders has recently spent a sabbatical leave.

The accepted idea is that the working medium which absorbs energy and releases it should be a gas: no solid would have the optical uniformity needed. Energy would be

pumped in by an electric discharge, by an intense light source, by electron bombardment, or by some other means. Simply to do that would make the gas glow in an unexciting manner: for a maser the important addition would be a pair of exceptionally flat glass plates, with reflecting surfaces, arranged on either side of the gas chamber.

Light emitted by the gas would zigzag between the plates and escape at the edges—all except for that light which happened to be traveling exactly along a path at right angles to the two mirrors. That would remain in the system, and would stimulate the emission of more light from gas along the same paths. Almost instantaneously, after switching on the pumping energy, the gas would be radiating very intense energy at right angles to the mirrors. If it had been arranged that one of the mirrors was slightly transparent, the light would emerge as a powerful parallel beam.

In July 1960 announcement was made of the successful development in the United States of an optical maser (or *laser*, from the initials of light amplification by stimulated emission of radiation) by Dr. T. H. Maiman of the Hughes Aircraft Co. As in the case of the microwave maser, a synthetic ruby crystal is used. A powerful light source such as a flash tube lamp is made to irradiate such a crystal. The light energy from the lamp with random or non-coherent waves excites the atoms in the crystal, and they in turn re-radiate light energy in an extremely narrow band of frequencies. The excited atoms are coupled in an atomic resonance and stimulated to emit the radiation with all waves coherent or in phase. The consequences are: (1) true amplification of light for the first time in history; (2) focusing of light into a high intensity beam for space communications (a beam of light directed at the earth from a laser on a satellite 1000 miles up could be concentrated in an area about 200 miles wide for taking sharp, detailed pictures); (3) a new tool for investigating the properties of

* Based on news items in *The New Scientist*, 7, 1185 (May 12, 1960); *Denver Post*, July 20, 1960.

matter; (4) vast increase in number of communication channels; (5) very high concentration of light which could generate intense local heat, for industrial, chemical, and medical purposes, such as modification and sterilization of surfaces.

G. L. CLARK

OPTICAL QUALITIES OF SPECTROSCOPIC INSTRUMENTS

Fundamental Concepts

The three most important optical specifications for any spectroscopic instrument are its dispersion (or optical purity), its resolution, and its speed or light-gathering power.

Dispersion. The *angular dispersion* may be written as $d\theta/d\lambda$, $\Delta\theta/\Delta\lambda$, or $(\theta_1 - \theta_2)/(\lambda_1 - \lambda_2)$, the difference in the angle of deviation, θ , for two rays of wavelength λ_1 and λ_2 . The linear dispersion, $\Delta l/\Delta\lambda$, is taken as a measure of the linear separation of the two lines in the focal plane of an instrument. In emission spectrochemical analysis it has become common practice to specify the *reciprocal linear dispersion*, (or *plate factor*), $\Delta\lambda/\Delta l$, as the measure of dispersion. This is normally expressed as Å/mm, that is, the difference in the wavelengths of two lines in Å, divided by the observed separation of these lines on the plate, in mm. Unfortunately, this usage can be confusing, in that a spectrograph with a dispersion of 5 Å/mm is twice as powerful as one with 10.

In a monochromator or spectrophotometer the *spectral purity* or *spectral band width* is commonly used as a measure of dispersion. It is the wavelength range transmitted by the use of specified entrance and exit slit widths, so that a monochromator having a reciprocal linear dispersion of 40 Å/mm in the focal plane will yield a spectral purity of 4 Å, or 4 millimicron, using slits of 0.1 mm.

Resolution. The *resolution* of any spectroscopic instrument is defined as $\lambda/\Delta\lambda$,

where $\Delta\lambda$ is the wavelength separation of two lines just distinguishable as two, and λ is their average wavelength.

Lord Rayleigh¹ suggested that two lines might be defined as resolved if the central maximum of the diffraction pattern of the slit for the first line falls at the first minimum of the diffraction pattern of the other, as indicated in Figure 1. This diagram shows the intensity distribution across the two images, formed by a perfect optical system, limited only by diffraction. The condition for achieving such a diffraction pattern is illustrated for any spectroscopic instrument in Figure 2, where light from a slit S is collimated by a lens L_1 , is spread into a spectrum by some dispersing element whose width is AB , and is imaged at a focal curve PP' by a second objective lens L_2 . It is assumed that L_1 , L_2 and any condensing lenses ahead of S_1 illuminate and transmit the full width AB and that all optical elements are perfect, so that the quality of the image is determined by diffraction limitations only.

At point P , which is chosen on the optical axis, a ray thought of as originating at A by Huyguens' construction, will travel

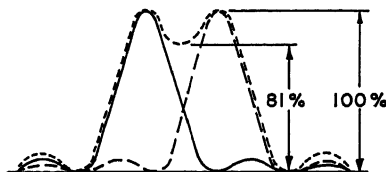


FIG. 1. Conditions for the resolution of the diffraction patterns of two slits, according to Rayleigh's criterion.

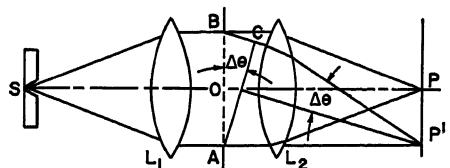


FIG. 2. Formation of diffraction pattern from an aperture of width $AB = W$. (From "Experimental Spectroscopy," Ralph A. Sawyer, 2nd Ed., Prentice-Hall, Inc., 1951)

exactly as far as the ray from B . Similarly, rays from any other point in the upper half AO of the aperture AB will travel exactly as far as the corresponding ray in the lower half BO . Accordingly, at P there is constructive interference and the intensity will be a maximum. P' is a point at an angle $\Delta\theta$ from P such that the difference between the rays from A and B to P' , that is, the distance BC , is exactly one wavelength, λ . This means that the ray A will be just $\frac{1}{2}\lambda$ different from the ray from O . Similarly, every other ray from the upper half AO will be just $\frac{1}{2}\lambda$ different from the corresponding ray in the lower half. This means that at P' there is destructive interference and an intensity minimum. Accordingly, the figure represents the condition specified by the Rayleigh criterion and directly from the construction we see that

$$\Delta\theta = \frac{\lambda}{AB}.$$

Since we can write the resolving power $\lambda/\Delta\lambda$ as

$$\frac{\lambda}{\Delta\lambda} = \frac{\lambda}{\Delta\theta} \cdot \frac{\Delta\theta}{\Delta\lambda}$$

and can substitute in this expression $\Delta\theta$ derived above, we can obtain the fundamental equation,

$$\frac{\lambda}{\Delta\lambda} = AB \frac{\Delta\theta}{\Delta\lambda},$$

or

$$\frac{\lambda}{\Delta\lambda} = w \frac{d\theta}{d\lambda}. \quad (1)$$

This shows that the fundamental resolution of any dispersing device is limited only by its effective width and its angular dispersive power.

In practice, the resolution or what we may call the "working resolution" of a spectroscopic instrument is determined by many factors, including particularly:

(1) The criterion considered adequate for calling two lines resolved.

(2) The quality of the illumination—whether it is on axis and fully illuminates the dispersing device and whether it is coherent (a point source at a distance without lenses) or incoherent (as though the slit were self-luminous) or a mixture (the normal situation with a condensing lens).

(3) The quality of the optical imaging elements (lenses or mirrors).

(4) The quality of the dispersing device.

(5) The aberrations of the over-all optical design.

(6) The adjustment of the optics for best focus.

(7) The slit width, at the dispersion employed.

(8) The resolution of the detector—the photographic plate, at the density of the exposure (and the resolution of the microphotometer or viewing lens used to evaluate it), the viewing eyepiece of a spectroscope, the exit slit and photodetector of a spectrometer.

(9) The relative intensities of the two lines.

(10) The natural widths of the spectrum lines emitted by the source itself.

Unfortunately, there is no common agreement even on the definition of "working resolution," and it is not a simple quality to define. To illustrate, should the two lines 3072.063 Å, 3072.009 Å in the curve of Figure 3 be considered as resolved? They certainly do not show an intensity drop of 19% between the peaks, as prescribed by the Rayleigh criterion, but they do appear as two lines. If they are resolved, the working resolution of the instrument is 3072/.054, or 57,000. If the *half width* of the sharpest line, that is, the width of the line at half its height, is accepted as $\Delta\lambda$, the resolution may be increased to 70,000, whereas if a 19% intensity drop is insisted upon, then the lines 3070.392 Å, 3070.318 Å become more appropriate, and the resolution falls to 42,000. By selecting the appropriate criterion, it is possible to show that the actual

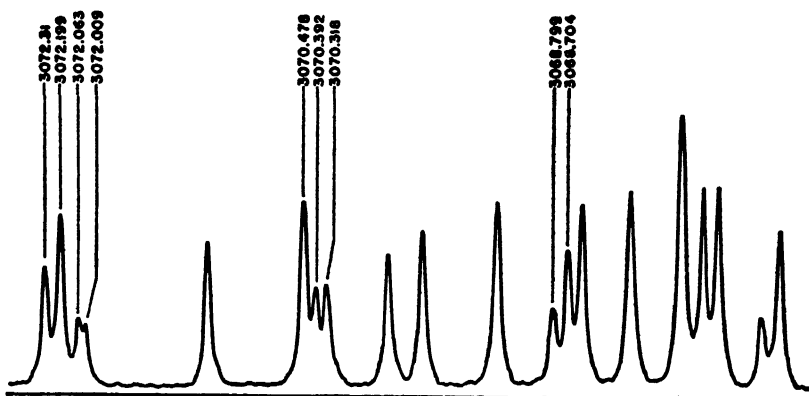


Fig. 3. Second-order spectrum at 3070 Å region of OH emission from a bunsen flame. (Courtesy National Bureau of Standards) (From "A Small Plane Grating Monochromator, William G. Fastie, *J. of the Optical Society of America*, 42, No. 9, 641-647, 1952)

resolution of an instrument equals, or even exceeds, the "theoretical" resolving power.

In the above list of factors which affect working resolution, only (3), (4) and (5) depend on the optical quality of the instrument itself. The other factors are under the control of the operator. In many cases the resolution of the instrument itself is considerably greater than the working resolution actually achieved. Figure 4 and Tables 1 and 2 illustrate how factors (7) through (10) can, in practice, determine the working resolution. The figures all show the Fe "triplet" (only three lines could be resolved by commercial spectrographs twenty years ago) at 3100 Å. The two lines 3099.897 Å, 3099.971 Å are .074 Å apart, and require a resolution of 44,000 to separate.

The asterisks in Table 2 indicate the controlling factor in determining the resolution. It is noteworthy that in each case some factor other than instrumental performance sets the limit on resolution. Only in the first order case is the instrumental limitation approached, and this was achieved only by employing a special high resolution source and a slit so narrow as to be useless for accurate quantitative measurements. Indeed, the need for compactness in laboratory equipment normally means that dispersion rather than resolving power is the limiting

factor which determines working resolution. This is particularly true if quantitative measurements are to be made; when wider slits, usually in the range 10-50 μ , must be employed to obtain accurate photometric measurements. Fortunately, a working resolution of 10,000-30,000 is ample for much practical work.

It is obvious that claims of manufacturers for high resolving power need to be examined for the specific details of the exposure before being accepted as indicating an ability to meet exacting resolution requirements.

Critical and Empty Dispersion. When the width of the spectrum line is determined by the breadth of the line emitted by the source rather than by the diffraction-broadened image of the slit, we are employing "empty dispersion." R. F. Jarrell has stated on theoretical grounds and R. K. Brehm has demonstrated empirically that as the dispersion is increased to a *critical dispersion* at which the slit and line widths are equal, the analytical limit of detection improves; but as increasingly empty dispersion is used, the line-to-background ratio actually falls and the sensitivity is reduced.

The case of the 3-ampere d.c. arc photographed in the seventh order with a 10 μ slit at a dispersion of 1.4 Å/mm illustrates such a condition, at least for analytical

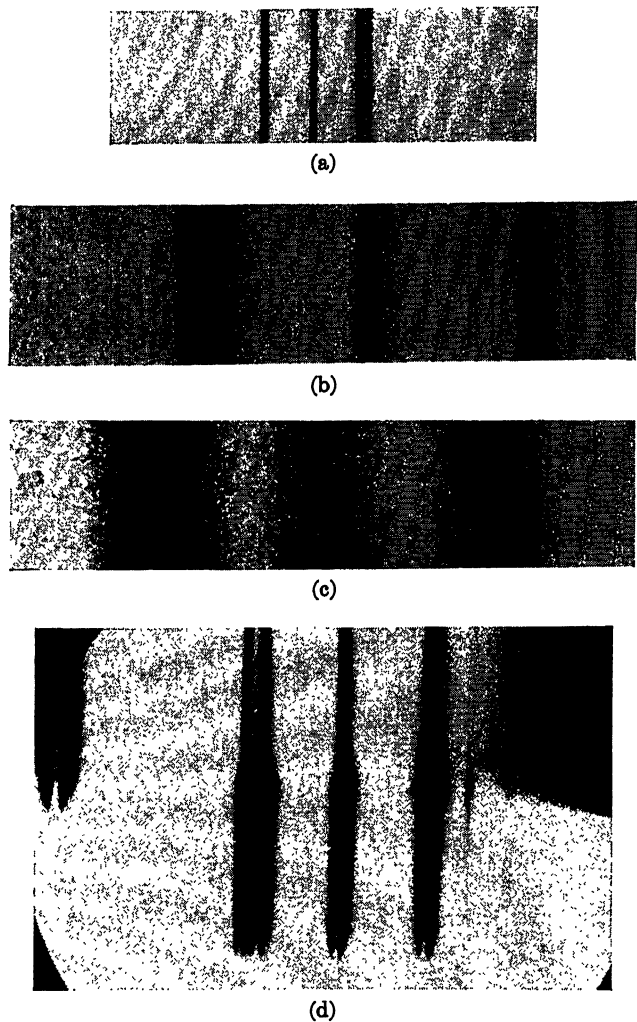


FIG. 4. Examples of resolution (see Table 1).

TABLE 1. CONDITIONS OF EXPOSURE

Instrument Employed	Jarrell-Ash 3.4 Meter Ebert Spectrograph, 1st Order, 15,000 Grooves/Inch	Jarrell-Ash 3.4 Meter Wadsworth Spectrograph, 2nd Order, 15,000 Grooves/Inch		Jarrell-Ash Ebert Spectrograph, With Order Sorter, 7th Order, 7500 Grooves/Inch
Dispersion	Fig. 4(a) 5.0 A/mm	Fig. 4(b) 2.4 A/mm	Fig. 4(c) 2.4 A/mm	Fig. 4(d) 1.4 A/mm
Slit width	5 μ	10 μ	30 μ	10 μ
Approximate density of lines	.35	.6		1.0
Approximate γ of plate	1.8	1.5		1.5
Resultant resolution of plate, lines/mm	100	40		40
Light source	hollow cathode .090 amp	dc iron arc 1.0 amp		dc iron arc 1.0 amp 3.0 amp

OPTICAL QUALITIES OF SPECTROSCOPIC INSTRUMENTS

TABLE 2. LIMITATIONS ON RESOLUTION
All data expressed in Angstroms

Instrument Employed	Jarrell-Ash 3.4 Meter Ebert Spectrograph, 1st Order, 15,00 Grooves/Inch	Jarrell-Ash 3.4 Meter Wadsworth Spectrograph, 2nd Order, 15,000 Grooves/Inch		Jarrell-Ash Ebert Spectrograph, With Order Sorter, 7th Order, 7500 Grooves/Inch	
Diffraction Broadening (Theoretical Resolution)	.041	.021	.021	.012	.012
Slit Width at Dispersion Employed	.025	.024	.07*	.014	.014
Photographic Emulsion at Density Level and γ of Negative	.05*	.06*	.06	.03*	.03
Resolution Imposed by Microphotometer 10 μ	.05*	.025	.025	.025	.025
Width of Spectrum Line	.01	.03	.03	.03*	.06*
Over-all Working Resolution	.07	.06	.08	.03	.06
Equivalent Resolving Power	44,000	51,000	39,000	103,000	51,000
Per cent of Theoretical	55%	34%	26%	39%	19%

purposes. A dispersion of 5 A/mm would be adequate. The dispersion of 1.4 A/mm would not be empty if the slit width were increased to about 24 μ , or if the spectrogram were to be used to study self-reversal or line shape.

Speed. Over the last twenty years various photoreceptors have been employed more and more frequently to measure directly the output of spectroscopic instruments. Prior to that time, the eye or the photographic emulsion (or small thermopiles) had been utilized. It is not sufficiently appreciated that there is a marked difference between these traditional detectors and the large area photoreceptors. Both the eye and the photo-

graphic plate require a minimum level of *illumination* to produce a detectable response. The phototube, multiplier phototube, barrier layer photocell, Golay cell, many photoconductive cells and thermopiles, and any other receiver in which the photosensitive surface is larger than the exit slit or exit slit image, all require a minimum total *flux* to produce a detectable response. Not until the area irradiated exceeds the photosensitive area do they become dependent on illumination.

A typical spectroscopic system is sketched schematically in Figure 5. A source, assumed to have a uniform brightness B (usually not justified), illuminates a slit, S , through a condensing lens, L_1 , which illuminates the full height of the slit and the entire area of the collimator L_2 . In this sketch, the angular deviation of the dispersing element, A , is not shown. The objective, L_3 , forms an image of the slit at P . Now if the aperture stop of the system is L_3 , and if L_3 is circular, then the illumination at P can be shown to depend only on $E' = \pi BT \sin^2 \theta'$,² where T is a transmission factor to take into account the reflection losses from surfaces and absorption within the optical elements, and θ' is the angle subtended at P by the objective. In other words, in this idealized case the visual or photographic speed of a spectroscope or spectrograph depends only on the brightness of the source, the transmission of the optics, and the size of the pencil of rays converging at the image.

Since the angle subtended by the objective is usually less than 15° , $\sin \theta' = \tan \theta' = d/f$, where d is the diameter of the objective and f is its focal length; f/d is the familiar expression for the aperture ratio or f /number used

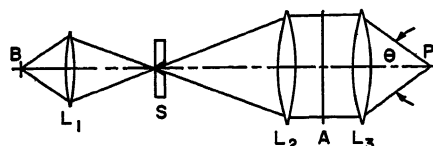


FIG. 5. Illumination in a spectrograph.

to designate the speed of a photographic lens. So for this idealized case we may write

$$E' = BT \frac{1}{(f/\text{number})^2} \quad (2)$$

Aperture Ratio and Effective Aperture Ratio. In spectroscopic instrumentation it is ordinarily not good design practice to have the objective constitute the aperture stop, because normally the dispersing element is inherently more expensive. A prism requires a larger optical blank than an objective lens of equal effective cross section. A grating is usually more expensive than the objective used with it. Accordingly, good usage makes the dispersing element serve as the aperture stop. Prisms are usually produced with a height equivalent to the effective width (the actual width of the face multiplied by the cosine of the angle of incidence), so that the effective cross section is a square. The ruled area of a grating is usually wide for good resolution but relatively short, to reduce astigmatism, so that the effective area is rectangular.

For such rectangular aperture stops, the photographic or visual speed of the spectroscopic system can be expressed in terms of the effective aperture ratio, defined as: effective aperture ratio = f/d' , where d' is the effective diameter;

$$d' = 2 \sqrt{\frac{hw \cos i}{\pi}},$$

where h is the height of the prism or grating ruling, w is its width, and i is the angle of incidence.

The relative speeds of two spectroscopes or spectrographs will, therefore, normally be in inverse proportion to the squares of their effective f /numbers. Where speed is a major consideration, as in a Raman spectrograph, it may be necessary to have a large dispersing element and an objective of large diameter and short focal length, to obtain the largest possible cone of illumination at P . This becomes expensive, and would be

doubly so if the collimating system also had to have a high aperture ratio. However, the collimator, while it must be roughly the same diameter, need not have a short focal length. This will usually be much less expensive and the optical aberrations will be smaller. We can see why this is so. If the collimator has a focal length three times greater than the objective, the spectrum line will be one-third the size of the slit. If a $20 \mu \times 2 \text{ mm}$ spectrum line is desired, a $60 \mu \times 6 \text{ mm}$ slit must be illuminated. If this can be done with the same level of illumination as a $20 \mu \times 2 \text{ mm}$ slit, it is obvious that the final image will be as bright, despite the longer focal length of the collimator, because all the energy is concentrated on $1/9$ th the area.

When the detector responds to the total flux incident on its photosensitive surface, a high aperture ratio is no longer important; instead the *light gathering power* or *flux transmitting power* becomes the controlling factor.

Flux Transmitting Power. The *flux transmitting power* of a spectroscopic instrument depends on:

(1) The effective transmission or efficiency of the optical elements, T .

(2) The effective area, $A = hw \cos i$, and angular dispersive power $d\theta/d\lambda$ of the dispersing element.

(3) l/f , the ratio of the maximum slit height which can be used for a critical problem without destroying the spectral purity, divided by the focal length.

$$F = kT \frac{l}{f} A \frac{d\theta^*}{d\lambda} \quad (3)$$

To understand the difference between speed and flux transmitting power, consider the relative performance of two Ebert monochromators, M_1 and M_2 , which have similar gratings of 15,000 grooves/inch, 65 % efficiency for Hg 2537 Å, the wavelength of interest, and ruled areas of $52 \times 52 \text{ mm}$, which are the limiting apertures. M_2 has a focal length of 1000 mm, M_1 of 500 mm. For 2537 Å, i will be about 9° .

* See Ref. 3.

The relative speeds are inversely proportional to the squares of the effective f /numbers, so that M_1 photographically or visually will be four times faster.

$$\begin{aligned} \frac{I_1}{I_2} &= \frac{(\text{effective } f/\text{number}_2)^2}{(\text{effective } f/\text{number}_1)^2} \\ &= \frac{\left(\frac{f_2}{(2\sqrt{h_2 w_2 \cos i_2})/\pi} \right)^2}{\left(\frac{f_1}{(2\sqrt{h_1 w_1 \cos i_1})/\pi} \right)^2} \\ &= \frac{\left(\frac{1000}{(2\sqrt{52 \times 52 \times .988})/\pi} \right)^2}{\left(\frac{500}{(2\sqrt{52 \times 52 \times .988})/\pi} \right)^2} \\ &= \frac{(17.2)^2}{(8.6)^2} = 4/1 \end{aligned}$$

However, the linear dispersion of M_2 will be twice that of M_1 — .06 mm/A *vs.* .03 mm/A, so that the entrance and exit slit widths of M_2 may be doubled to maintain the same spectral purity. Also, the slit height may be at least doubled without affecting the resolution, say, from 5 mm to 10 mm. Accordingly, the entrance slit of M_2 can admit four times as much flux for Hg 2537 as the slit for M_1 , and this energy will be transmitted by the exit slit, spread over a four times larger area. If we are using a photomultiplier tube or other photoreceptor, the same signal will be produced by M_1 and M_2 , and the flux transmitting power will be the same.

$$\begin{aligned} \frac{F_1}{F_2} &= \frac{T_1 L_1 / f_1 A_1 (d\theta/d\lambda)_1}{T_2 L_2 / f_2 A_2 (d\theta/d\lambda)_2} \\ &= \frac{.65 \times 5/500 \times 52 \times 52 \times 5.9 \times 10^{-6}}{.65 \times 10/1000 \times 52 \times 52 \times 5.9 \times 10^{-6}} = 1 \end{aligned}$$

where $d\theta/d\lambda = 1/b$ expressed in radians/A.

On the other hand, assume that M_2 has a grating of 104×104 mm (i.e., the aberrations of the two instruments remain constant). Furthermore, assume that the grating of M_2 has 30,000 grooves per inch, compared to 15,000 grooves per inch for M_1 , so that

its angular dispersion is double, with the same efficiency, 65 %. Now both instruments have effective f /numbers of $f/8.6$, so that the illumination at the exit slit is the same in both cases; however the linear dispersion of M_2 is .12 mm/A, so that to retain the same spectral purity the slit width may be quadrupled and the height may be doubled. Thus, the flux transmitting power will be eight times as great as M_1 .

If M_1 is equipped with straight slits which limit the slit height for the resolution desired to 5 mm, and M_2 has curved slits, permitting a slit height not merely of 10 mm but of 30 mm for the same resolution (assuming that 30 mm may be illuminated as intensely as 10 mm), then the flux transmitting power of M_2 becomes twenty-four times that of M_1 .

To intercompare monochromators for flux transmitting power it is necessary to specify the spectral purity required for a particular problem, because this may establish the permissible slit height resulting from the aberrations of the system. This is particularly true in a prism monochromator, where the curvature of the spectral lines is markedly dependent on wavelength, and in grating monochromators when straight slits are used in Ebert or Czerny-Turner mountings. A spectral purity of .1 A may require the use of slits only 1 mm high, whereas a spectral purity of .2 A may impose no limitation at all on the slit height, which can be used at its physical limit. A comparison of the flux transmitting power and f /numbers of some typical monochromators is given in Table 3, assuming a spectral purity of .2 A.

Critical Slit Width or Optimum Slit Width. Both theoretical calculations and experimental data show that when the slit of a spectrograph is narrowed beyond a certain limit, the illumination drops very rapidly, while the resolution is improved only slightly. This point is called the critical slit width and can be calculated from the equation $C.W. = \lambda f/D$, where λ is the wave-

EMISSION SPECTROSCOPY—LIGHT

TABLE 3. FLUX-TRANSMITTING POWERS AND f /NUMBERS OF TYPICAL SPECTROMETERS

Instrument	T	h	$W \cos i$	$d\theta/d\lambda$	L/f	F^*	Effective f /Number
An $f/4.5$ Quartz Prism Monochromator, 60° Prism, Double Passed	.59	70	40	1.48×10^{-4}	1/270	9.0	4.5
Ebert $f/8$ Plane Grating Monochromator, 500 mm, 30,000 g/in Curved Slits	.52	52	50	1.18×10^{-4}	20/500	64	8.8
Ebert 1.8 Meter Spectrometer, 30,000 g/in	.52	125	135	1.18×10^{-4}	100/1800	558	12.3
Medium Quartz Spectrograph	.69	41	41	7.42×10^{-5}	2/540	3.2	11.7
Concave Grating Direct Reading Spectrometer, 1.5 Meter, 30,000 g/in	.65	41	54	1.18×10^{-4}	20/1300	26	24.5
Large Littrow Quartz Prism Spectrograph	.63	56	56	7.42×10^{-5}	5/1700	4.3	27.0
Large Grating Spectrograph, 30,000 g/in	.52	57	125	1.18×10^{-4}	20/3360	26	35.0

T is the over-all transmittance of the system, assuming that a lens has a transmission of 90%, and a prism 85%, that a mirror has a reflectivity of 90% and that the efficiency of a grating near its blaze is 65%.

h is the height of the dispersing element.

$W \cos i$ is the effective width of the dispersing element.

$d\theta/d\lambda$ is the angular dispersive power.

L is the height of slit permissible to achieve .2 A half intensity band width.

f is the focal distance.

* All values of F have been multiplied by 10^4 to produce more convenient values.

length, f the focal length, and D the diameter of the collimator.

Thus, the critical slit width on an $f/30$ spectrograph for the 5890 A line of sodium would be $.589 \times 30$ or 18μ .

Action of a Prism

Theory. The action of a prism depends on the refraction of light by the prism material or, more precisely, on the dispersive power of the material, that is, on the variation of

the index of refraction with wavelength. As a light ray enters a transparent material at an angle of incidence, i , it will be bent toward the normal, according to Snell's law, so that $n_1 \sin i = n_2 \sin r$, where n_1 and n_2 are the indices of refraction of the initial and secondary media, and i and r are the angles of incidence and refraction (Figure 6).

The ray is deviated from its original course because of its interaction with the oscillators present in the crystal structure of the medium. This interaction must be slight or the light would be absorbed and the medium would not be transparent. For all materials transparent in the visible, the oscillators must have natural frequencies in the ultraviolet and infrared. Toward the ultraviolet, as the frequency increases, the interaction between the incoming beam and the oscillators of the material becomes greater, and the ray is more and more strongly deviated.

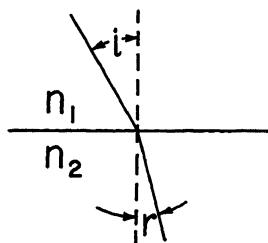


FIG. 6. Snell's Law.

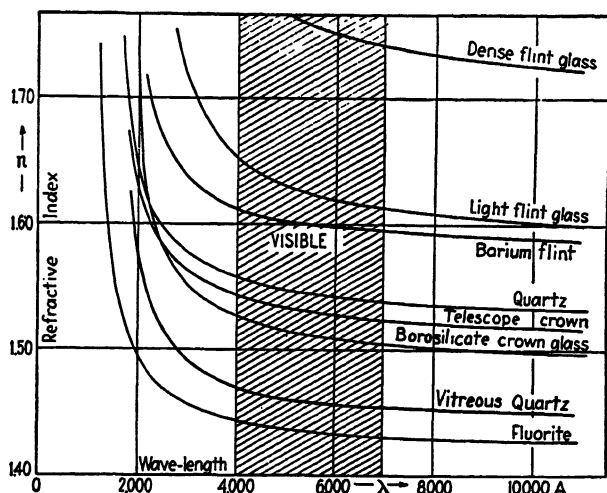


FIG. 7. Dispersion curves for several different materials commonly used for lenses and prisms. (From "Fundamentals of Optics," 2nd Ed., F. A. Jenkins and Harvey E. White, McGraw-Hill Book Co., 1950)

Typical curves of index of refraction versus wavelength are given in Figure 7.

It is obvious that the dispersive power of a material becomes better toward the ultraviolet. Indeed, it becomes best as the natural frequency of the oscillators of the material is approached, and at this point the material becomes opaque because of absorption. Because of this fundamental characteristic of optical materials, all prism spectrographs, in going toward the ultraviolet, exhibit:

- (1) a shorter focal length
- (2) higher dispersion
- (3) increasing absorption

Two empirical formulas have been derived to represent the observed variation of refractive index. In 1836 Cauchy proposed the formula $n = A + B/\lambda^2 + C/\lambda^4$, where n is the refractive index, λ the wavelength and A , B and C are constants for a given material.

Hartman⁴ in 1898 proposed $n = n_0 + C/(\lambda - \lambda_0)$, where again n is the refractive index, λ the wavelength and n_0 , λ_0 and C are constants for the material. This formula, in the form $\lambda = \lambda_0 + C/(d_0 - d)$, or preferably⁵

$$\lambda = \lambda_0 + \frac{C}{(d_0 - d)^{1/2}}$$

where d_0 is a fiducial point and d is the distance of the line from that point, should always be employed to interpolate accurately between known wavelengths in prism spectra, particularly over any extended region.

Dispersion of a Prism. The astigmatism of a prism is least and the definition is best if the following conditions are observed:

- (a) The prism is illuminated by parallel light.
- (b) The slit is parallel to the prism edge.
- (c) The light rays pass through a plane parallel to the base.
- (d) The rays pass through the prism symmetrically, so that the incident and emergent beams form equal angles to the faces. The prism is then used at "minimum deviation."

Figure 8 shows a prism at minimum deviation. From Snell's law we obtain

$$n = \frac{\sin i}{\sin r'} = \frac{\sin \frac{\theta + A}{2}}{\sin \frac{A}{2}} \quad (5)$$

where A is the apex angle and θ is the angle of deviation. To obtain the angular dispersion $d\theta/d\lambda = (d\theta/dn) \cdot (dn/d\lambda)$ we differ-

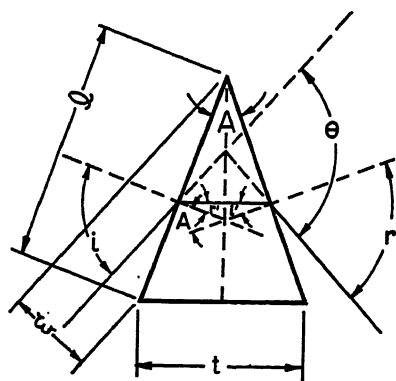


FIG. 8. A prism at minimum deviation.

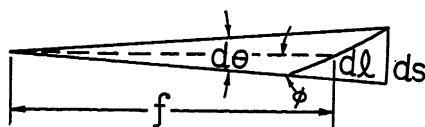


FIG. 9. Linear dispersion of a prism spectrograph.

entiate the equation above for n as a function of θ and the Hartman formula for n as a function of λ ; making the proper substitutions, we have:

$$\frac{d\theta}{d\lambda} = \frac{2 \sin A/2}{\sqrt{1 - n^2 \sin^2 A/2}} \cdot \frac{-C}{(\lambda - \lambda_0)^2} \quad (6)$$

or in another form:

$$\frac{d\theta}{d\lambda} = \frac{2 \tan i}{n} \cdot \frac{dn}{d\lambda} = \frac{2 \tan i}{n} \cdot \frac{-C}{(\lambda - \lambda_0)^2} \quad (7)$$

Usually the function desired is the linear dispersion $dl/d\lambda$, or, as it is now more commonly expressed, the reciprocal linear dispersion, $d\lambda/dl$ in Å/mm. As Figure 9 shows, this depends on the focal length of the spectrograph for that particular wavelength, (f), and on the angle which the plate makes to the emergent beam (ϕ),

$$\frac{d\lambda}{dl} = \frac{d\lambda}{ds/\sin \phi} = \sin \phi \cdot \frac{d\lambda}{f d\theta}$$

so:

$$\frac{d\lambda}{dl} = \frac{\sin \phi}{f} \left[\frac{\sqrt{1 - n^2 \sin^2 A/2}}{2 \sin A/2} \cdot \frac{(\lambda - \lambda_0)^2}{-C} \right] \quad (8)$$

The use of these equations is illustrated by the following example. The International

Critical Tables give for the index of refraction for the ordinary ray through crystal quartz the following data:

Wavelength	Index of Refraction
2573	1.59625
2749	1.58753
3611	1.56347

Substituting these values in the equation $n = n_0 + C/(\lambda - \lambda_0)$ and solving, we obtain $n_0 = 1.52110$, $C = 100.90$ and $\lambda_0 = 1230$ Å.

To find the reciprocal linear dispersion at 3100 Å for a Littrow quartz spectrograph for which the focal length at 3100 Å is 1650 mm, the apex angle of the prism 30° (but used twice so that it is equivalent to 60°) and the angle of the plate to the emergent beam 26° , we calculate first the index of refraction from

$$n = n_0 + \frac{C}{\lambda - \lambda_0} = 1.52110 + \frac{100.9}{3100 - 1230} = 1.57510.$$

Then we calculate the dispersion as

$$\begin{aligned} \frac{d\lambda}{dl} &= \frac{\sin \phi \sqrt{1 - n^2 \sin^2 A/2}}{f \cdot 2 \sin A/2} \cdot \frac{(\lambda - \lambda_0)^2}{-C} \\ &= \frac{.439}{1650} \cdot \frac{\sqrt{1 - 1.57510^2 \sin^2 30^\circ}}{2 \sin 30^\circ} \cdot \frac{(3100 - 1230)^2}{100.9} \\ &= 5.7 \text{ Å/mm.} \end{aligned}$$

The dispersion of a train of prisms is equal to the sum of the dispersions of the individual prisms.

Resolving Power of a Prism. From the general discussion of resolution we can write,

$$R = w \frac{d\theta}{d\lambda} = w \frac{d\theta}{dn} \cdot \frac{dn}{d\lambda}$$

where w is the effective width of the dispersing element, $w = l \cos i$ (Fig. 8). By differentiating equation (1)

$$\begin{aligned} \frac{d\theta}{dn} &= \frac{2 \sin A/2}{\sqrt{1 - n^2 \sin^2 A/2}} = \frac{2 \sin A/2}{\sqrt{1 - \sin^2 i}} \\ &= \frac{2 \sin A/2}{\cos i} \end{aligned}$$

Substituting, we have

$$w \frac{d\theta}{dn} \cdot \frac{dn}{d\lambda} = (l \cos i) \frac{(2 \sin A/2)}{(\cos i)} \cdot \frac{dn}{d\lambda} = t \frac{dn}{d\lambda}$$

So, for a prism

$$R = t \frac{dn}{d\lambda} \quad (9)$$

where t is the thickness of the base and $dn/d\lambda$ is the dispersive power of the prism material.

The resolution of a train of prisms is equal to the sum of the resolutions of the individual prism.

Curvature of Lines. The spectrum lines of prism instruments are curved, with a radius of curvature given by:

$$r = \frac{n^2 f}{2(n^2 - 1)} \cot i,$$

where n is the refractive index, f is the focal length of the camera lens and i is the angle of incidence. The lines are more curved toward the ultraviolet.

Action of a Grating

The Diffraction Pattern of Multiple Slits. If, in a typical spectroscopic system, we place a series of "diffraction gratings" composed of one, two, three or more equidistant slits, and use a filter to obtain monochromatic light from a mercury lamp or other simple line source, we can photograph patterns such as those shown in Figure 10. The first pattern shows the high-intensity central maximum and two weaker wings characteristic of diffraction from a narrow rectangular aperture or slit. As the number of slits is increased, the central maximum of this diffraction pattern breaks up into a number of lines which become progressively sharper. These lines are images of the primary spectroscopy slit by the "diffraction grating". In a practical grating for spectroscopic use the number of lines must be increased into the thousands and the spacing made very fine, usually of the order of 2500 to 30,000 to the inch. The individual slit

images in Figure 10f above then become truly sharp and monochromatic and the secondary maxima between disappear entirely. In Figure 10f the individual lines represent the central image and the first, second and third orders of Hg 4358 Å, on either side of the "central image," the undeviated ray.

The Grating Formula. The action of a reflection grating can be visualized more clearly from Figure 11. If the two incoming rays R_1 and R_2 form a plane wavefront, as the wave reaches the grating, R_2 must go further than R_1 by the distance $b \sin i$, where i is the angle of incidence. In leaving the grating R_1 must go further than R_2 by $b \sin r$, where r is the angle of reflectance. If the net path difference for the two rays, $b \sin i - b \sin r$, is equal to an integral multiple of a wavelength, $n\lambda$, rays R_1 and R_2 will be in phase and there will be constructive interference at the angle r . If the grating is used in a mounting such that the angles of incidence and refraction are on the same side of the grating normal (frequently then $r = i$), ray R_2 will have had to travel further than R_1 , both as it arrives at the grating and as it departs, so that the net path difference becomes $b \sin i + b \sin r$. The same argument can be applied to a transmission grating. The conditions for constructive interference give directly the familiar grating formula:

$$n\lambda = b (\sin i \pm \sin r) \quad (10)$$

where n is the order of interference, and b is the grating constant (expressed in Angstroms, microns, or millimicrons, i.e., 16,930 Å for a grating of 15,000 grooves/inch). The positive sign applies where incoming and emergent beams are on the same side of the grating normal.

Dispersion of a Grating. By differentiating the grating formula (10), we obtain immediately for the angular dispersion of a grating:

$$\frac{d\theta}{d\lambda} = \frac{dr}{d\lambda} = \frac{n}{b \cos r}$$

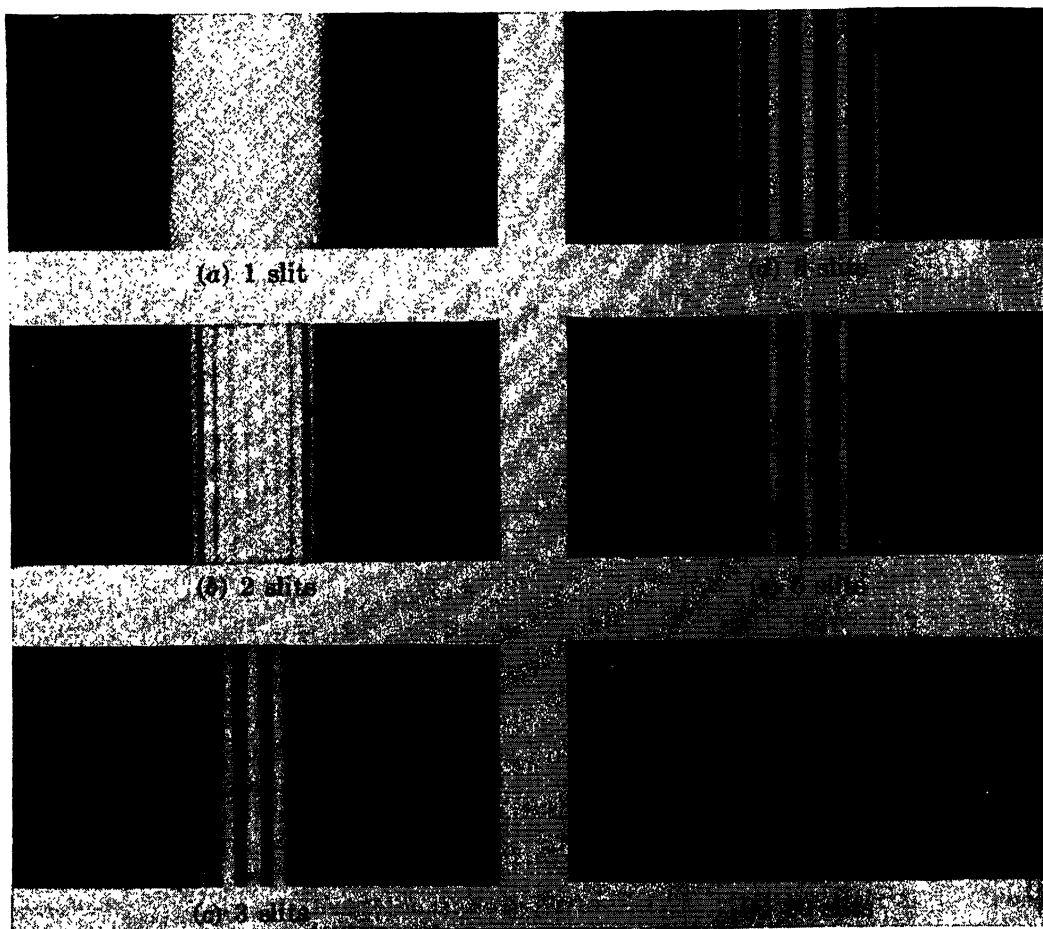


FIG. 10. Fraunhofer diffraction patterns for gratings containing 1, 2, 3, 5, 6, and 20 equidistant slits. (From "Fundamentals of Optics," 2nd Ed., F. A. Jenkins and Harvey E. White, McGraw-Hill Book Co., 1950)

From the grating normal, where $r = 0$, to 8° off the normal, $\cos r$ changes only from 1.00 to 0.99, so that $d\theta/d\lambda$ is nearly constant, equal to n/b . For this reason, viewing a grating on the normal results in linear dispersion. The reciprocal linear dispersion is given by:

$$\frac{d\lambda}{dl} = \frac{\sin \varphi}{f} \frac{d\lambda}{d\theta} = \frac{\sin \varphi b \cos r}{nf} \quad (11)$$

where, as in the prism case, φ is the angle between the central ray and the focal curve and f is the focal distance from the objective lens to the focal curve.

Resolving Power. From the fundamental equation (1)

$$R = w \frac{d\theta}{d\lambda}$$

where w , the effective aperture width, in the case of a grating can be written simply as the width of an individual ruling, b , multiplied by the total number of rulings, N , and by $\cos r$, i.e., $bN \cos r$. Since $d\theta/d\lambda = n/b \cos r$, we have immediately:

$$R = Nn. \quad (12)$$

The importance of the number of lines in

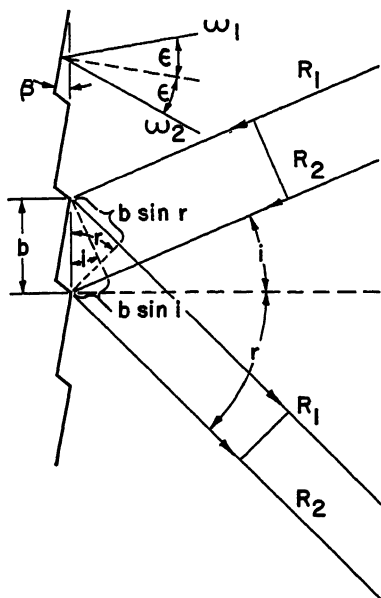


FIG. 11. Interference of rays from successive grooves of a reflection grating.

a grating has already been implied in the preceding discussion.

However, it should be emphasized that it is the product, Nn , that counts, so that a 6" grating of 30,000 grooves/inch, where N is 180,000, will have no better resolving power than a 6" grating of 7500 grooves/inch, where N is only 45,000, provided both gratings are used at the same angle; a line imaged by the finer grating in the first order will be produced by the second in the fourth order at the same dispersion and resolution. Indeed, the *only* significant difference is that the grating of 7500 grooves/inch will have four times as many orders at a given angle. The advantage of a finer ruling is merely that it permits a higher dispersion in the *first* order.

Rowland Ghosts. As the section on grating ruling describes, all gratings produced on mechanical engines have a sinusoidal variation in the spacing of the grooves, with a period equal to one revolution of the drive screw, or some fractional multiple. Such a grating will produce, instead of a completely

plane or perfectly spherical wavefront, a sinusoidal wavefront, as shown in Figure 12, the spacing of which is determined by the number of grooves in a revolution of the screw, P . Such a wavefront will produce not only the desired "parent" line, but also pairs of *Rowland ghosts*, symmetrically placed on either side by a distance equal to:

$$\Delta\lambda = \frac{n'\lambda}{nP}$$

where n' is the order number of the ghost line, λ is the wavelength of the parent line, n is the order of the parent line, and P is the number of grooves cut in one revolution of the spacing screw. The intensity of the ghosts is given by:

$$I_g = I_0 \frac{n^2}{4} \left(\frac{2\pi e}{b} \right)^2$$

where I_g is the intensity of the ghost, I_0 of the parent line, n is the order of the parent line, e is the total spacing error in a period, and b is the grating constant.

A practicing spectroscopist can identify the Rowland ghost structure of his particular grating by examining a heavily exposed simple spectrum, such as Hg or Cu. On each side of the heaviest lines, in equally spaced pairs, the Rowland ghosts will appear. There may be three or four on each side, of which the closest to the parent line is usually the strongest.

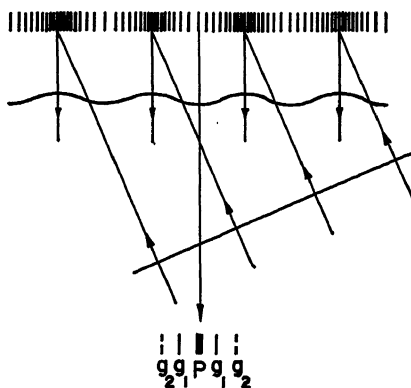


FIG. 12. Wavefront from a grating with a regular periodic error.

It will be noted that the ghost intensity increases with the order number (or, more fundamentally, with the angle of use of the grating). It is common practice for manufacturers to hold Rowland ghost intensities to less than $\frac{1}{1000}$ for the first order of a grating of 15,000 grooves/inch (600 grooves/cm). This corresponds to less than $\frac{1}{4000}$ in the first order for 7500 grooves/inch, or $\frac{1}{250}$ for 30,000 grooves/inch. (See also Gratings, Production of, p. 173).

Lyman Ghosts. Lyman ghosts are spurious lines produced by two periodic errors in the ruling engine interacting to produce lines which appear in the ultraviolet or infrared far removed from the parent line. Lyman ghosts in a grating can be detected by taking very heavy exposures of a monochromatic source, e.g., Hg 4358 Å isolated by a filter, and looking for weak lines in the ultraviolet or visible.

The spurious lines may appear in pairs or quartets, at a mean wavelength which should be some simple fraction of the parent line, for example, $\frac{2}{3}$, $\frac{3}{5}$, $\frac{4}{5}$, or at $\frac{2}{5}$, $\frac{1}{5}$, etc. Lyman ghosts are usually held well below $\frac{1}{10000}$ the intensity of the parent line, and hence are almost never detected in spectrochemical analysis.

Intensity Distribution of a Grating. Modern gratings are *blazed* to concentrate the radiation in a desired wavelength region. In a reflection grating the diamond is set to produce a groove which will act like a mi-

nute mirror to reflect light in the desired direction, as drawn in Figure 11 for rays w, w_2 .

The blaze angle, β , depends on the geometry of the application, and in the general case should be determined from a ray sketch. The relationships are simple in special cases.

In a Littrow or under-over Ebert mounting, where $i = r$, $\beta = i$. In a Rowland, Abney or Wadsworth concave mounting, where $r = \theta$, $\beta = i/2$.

At times, particularly in the coarser rulings, as much as 75 or 80 % of the radiation of a particular wavelength incident on the grating may be concentrated into a single order.

Since an individual groove of a grating may approach the wavelength of the light desired (for a grating of 30,000 grooves/inch the rulings are 8470 Å apart), it cannot be 100 % efficient, even if it were possible to control its shape exactly. Theoretically, the radiation reflected by the groove will have its blaze maximum in the direction of specular reflection, and for a particular wavelength the intensity distribution will be within the envelope set by the diffraction pattern of a single slit equal to the groove width. In other words, the distribution will be similar to Figure 1. For a groove of $.85 \mu$ and a wavelength of $.436 \mu$, the diffraction envelope will be very broad. For a wavelength of $.254 \mu$, the pattern will be narrower. If, for a particular groove angle, the patterns for different wavelengths are summed, the over-all intensity distribution will have a theoretical distribution as indicated in Figure 13. The reflectivity of a grating assumed to have 80 % efficiency at the blaze wavelength falls to 40 % at $\frac{2}{3}\lambda_m$ and $1\frac{1}{2}\lambda_m$.

From this discussion it should be obvious that the blaze of a grating is primarily a matter of direction. Accordingly, a ruling whose intensity peaks at 6000 Å in the first order will normally have its second order peaked at 3000 Å.

The intensity distribution found in real

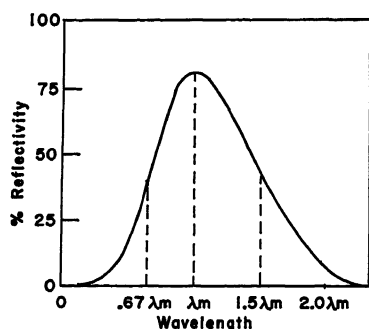


FIG. 13. Theoretical intensity distribution of a blazed grating.

gratings seldom conforms closely to the ideal, since the groove shape cannot be accurately controlled. Sometimes a ruling may turn out to have sub-spacing in small integral fractions. For example, the groove itself may occupy two-thirds of the spacing distance, while one-third of the surface is relatively unaffected. In such a grating the third order will be extremely weak.

The Concave Grating. H. A. Rowland,⁶ in 1882, was able to demonstrate theoretically and experimentally that if a concave mirror were ruled with "lines" spaced equally along the chord across its center, the resultant concave grating would produce spectra, in accordance with the standard grating formula. The concave grating requires no separate collimator or objective, since it is both a dispersing and focusing element. The focus for the spectrum from a concave grating is given by the formula:

$$\left(\frac{\cos i}{\rho} - \frac{\cos^2 i}{S} \right) + \left(\frac{\cos r}{\rho} - \frac{\cos^2 r}{S'} \right) = 0 \quad (13)$$

where i and r are the incident and reflected angles, ρ is the radius of curvature of the concave blank, S is the slit to grating distance, and S' is the distance from the grating to the image of the spectrum. This equation can be satisfied by setting $S = \rho \cos i$ and $S' = \rho \cos r$, the polar equations for a circle of diameter ρ , containing the points S , S' and G , as shown in Figure 14. This is the famous *Rowland circle*. (This is not the only possible solution to equation (13), but all others except that discussed later under the Wadsworth mounting lead to higher secondary aberrations.)

It should be noted that the grating is tangent to the circle at G , but does not conform to it. The radius of curvature of the grating is *not* the radius of the circle, but rather its *diameter*. (The *focal length* of the concave mirror as such is equal to the radius of the circle.)

Astigmatism of the Concave Grating. Unfortunately, the concave grating suffers

from *astigmatism*. A crosshair or the edge of a diaphragm, sector or stepped filter placed at the slit will not be in focus at S' . Instead, the focus for a horizontal object is given by the equation:

$$\left(\frac{1}{h} - \frac{\cos i}{\rho} \right) + \left(\frac{1}{h'} - \frac{\cos r}{\rho} \right) = 0 \quad (14)$$

where h and h' are the distances of the horizontal object and image from the grating, respectively. As a result of astigmatism the spectral image of a point slit consists of a vertical line at the focal curve, parallel to the grooves of the grating. When an extended slit is used, the spectral line consists of a whole series of overlapping line images of the individual points along the slit. Therefore, the slit must be aligned very exactly with the grating grooves to obtain maximum resolution.

The Wadsworth mounting of the concave grating, described later, most plane grating instruments, and all prism systems except the F ry are essentially *stigmatic*. Diaphragms, sectors or other devices placed at the slit will be sharply focused at the spectrum. Stigmatic spectrographs can be "crossed" with Fabry-Perot etalons, echelles or other interferometric dispersing elements.

Because of the astigmatism of Rowland circle mountings of the concave grating the illumination in the image depends on the length of the entrance slit. The slit height must be increased to the value:

$$l \left(\frac{\sin^2 r \cos i}{\cos r} + \sin^2 i \right)$$

where l is the height of the ruled grooves in order to obtain illumination equal to that of a stigmatic image.

Sirks' Focus. Sirks⁸ pointed out that if a horizontal object were placed outside the slit at the point where the optical axis intersected the tangent to the Rowland circle at S' , the image would fall at S' (see Figure 14, where H is the position of Sirks' focus).

In an astigmatic spectrograph the height of the spectrum is normally controlled by a

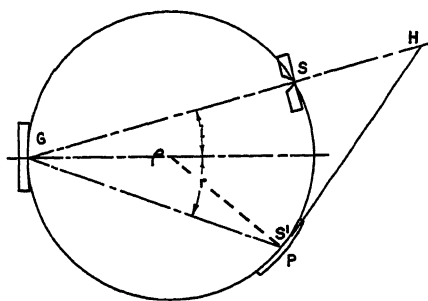


FIG. 14. Rowland circle focal curve of a concave grating.

diaphragm at the plateholder, and a comparison spectrum may be exposed by moving the diaphragm. However, stepped sectors or filters used for emulsion calibration must be placed at the Sirks' focus, which in the higher orders may become impractical because of the distance involved.

Wadsworth Concave Grating Mount.

Wadsworth⁹ pointed out that if $S = h = \infty$ and if $r = 0$, the two equations (13) and (14) have the same solution:

$$S' = h' = \frac{\rho}{1 + \cos i} \quad (15)$$

S and h may be made equivalent to ∞ by collimating the light by a concave mirror, which then illuminates the grating. r can be maintained at zero if the plateholder is mounted on the normal to the grating. When these two conditions are met, the image becomes stigmatic.

Interferometric Dispersing Elements

A grating has many grooves and the spectrum is formed by many individual rays

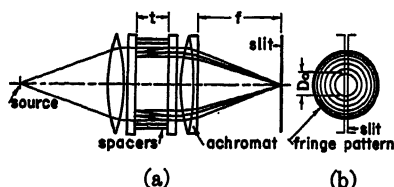


FIG. 15. (a) Arrangement of Fabry-Perot etalon in front of a spectrograph. (b) Appearance of interference fringes projected on slit.

whose path difference is one, two, three or some other small integral multiple of the wavelength. In the case of interferometric dispersing elements, a limited number of rays interact and the path difference amounts to thousands of wavelengths.

Fabry Perot Etalon. As an illustration of the action of an interferometer, consider the Fabry-Perot etalon, the most commonly used element of this type, shown in Figure 15. The Fabry-Perot etalon consists of two quartz or glass plates, one face of each worked very flat ($\frac{1}{20}$ th– $\frac{1}{100}$ th fringe), partially aluminized and separated by a spacer which renders the two faces exactly parallel. The outer faces form a small wedge angle with the working faces to prevent spurious fringes. Any ray entering the etalon will be reflected back and forth between the faces, and at each reflection some radiation will be transmitted. There will be some five to thirty successive transmitted rays, which result from a single incident ray, and these will be in a position to reinforce each other if the path distances between the two internal faces are integral multiples of the wavelength. The condition for obtaining a bright fringe will be given by $n\lambda = 2t \cos \theta = 2t$, approximately, since θ is small, (see Figure 15). Strictly, the pattern projected on the slit of the spectrograph will be a series of concentric, circular interference fringes governed by the relation:

$$n = \frac{2t}{\lambda} + \frac{2t}{\lambda} \left(\frac{D^2}{8f^2} \right) \quad (16)$$

where

n is the order of interference at the center of the ring system,
 t is the separation of the plates,
 D is the diameter of a particular ring of wavelength λ ,
 f is the focal length of the lens which projects the fringes on the slit.

The first term, $2t/\lambda$, represents the integral order of interference of the innermost ring

and the term

$$\frac{2t}{\lambda} \left(\frac{D^2}{8f^2} \right)$$

represents the fractional order between a ring of diameter D and the center.

Since the separation of the plates is not known to the required accuracy, t must first be determined by measurements on a known wavelength standard. Thereafter it becomes possible to measure the wavelengths of unknown lines to thousandths of an Angstrom, if the lines themselves are sufficiently sharp.

As the thickness of the aluminized or multiple-layer coating increases, the number of the reflections, and hence of the interfering rays, increases, so that the fringes become sharper. Since the absorption also becomes greater, the intensity of the pattern falls and there is a useful limit. 85%–90% reflectivity is generally considered the best compromise between high resolution and low intensity. Quantitatively, the resolving power is given by

$$\frac{\lambda}{d\lambda} = \frac{2\pi n}{\sqrt{4.45}} \cdot \frac{\sqrt{r}}{(1-r)} \sim n \cdot \frac{3\sqrt{r}}{1-r} \quad (17)$$

where $3\sqrt{r}/(1-r)$ can be considered physically as a measure of the effective number of interfering beams. In other words, $\lambda/d\lambda = Nn$, as with the grating.

For $\lambda = 5461$, $t = 10$ mm, $r = .9$, we have

$$\frac{\lambda}{d\lambda} = \frac{3\sqrt{.9}}{1-.9} \cdot \frac{2.0}{5.46 \times 10^{-5}} = 28\frac{1}{2} \cdot 36,700 = 1,045,000$$

In other words, for a reflectivity of 90%, we have effectively $28\frac{1}{2}$ interfering rays, with a path difference between successive rays, for a 10 mm separation of 36,700 wavelengths of 5461 Å, interfering to give a resolving power in excess of one million.

The Fabry-Perot etalon is a relatively simple device which, nevertheless, achieves the highest resolution of any known optical element. Wavelength measurements can be made to thousandths, or even ten thou-

sandths, of an Angstrom. The development of high reflectivity multilayer coatings which have relatively low absorption has greatly increased the effective speed of the Fabry-Perot etalon in recent years, and it is now used almost exclusively for ultra-high resolution work, displacing earlier devices described below.

The disadvantage of all such interferometric devices, using high order numbers, is the relatively limited *free spectral range*, that is, the wavelength range that can be covered in one order without overlapping lines from the next higher or lower order. For a Fabry-Perot interferometer, the free spectral range, expressed in Å, is given by $F_\lambda = \lambda^2/2t$, so that in the case above for Hg 5461,

$$F_\lambda = \frac{(5461)^2}{2 \times 10^3} = .15 \text{ Å.}$$

Thus a high dispersion, high resolution spectrograph is required to avoid overlapping orders in the Fabry-Perot pattern. In practice, a diameter of the ring pattern of the etalon is focused on the slit of a large spectrograph and some overlapping is tolerated for lines closer than 1 Å to 5 Å. High-resolution work with a Fabry-Perot etalon is an art, and the scientist undertaking such work should refer to the articles by K. W. Meissner in *Journal of the Optical Society of America*, starting with 31, 405 (1941) and 32, 185, (1942).

Fabry-Perot Interferometer. In the Fabry-Perot etalon described above, the separation of the plates is semipermanently fixed by spacers; the Fabry Perot interferometer has one plate fixed, the other adjustable. It can be used to measure short distances in terms of light waves.

Echelons. Transmission and reflection echelons are illustrated in Figures 16a and b. In transmission, the successive interfering beams have path differences equivalent to the thickness of the plates, expressed in wavelengths; in reflection, the path difference is merely $2t$. These devices were sug-

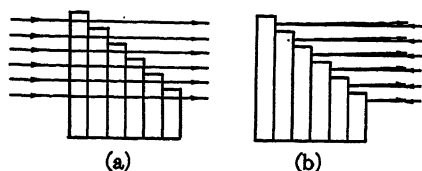


FIG. 16. (a) Transmission echelon. (b) Reflection echelon.

gested by Michelson, and the reflection echelon is particularly interesting because it can be used in the far ultraviolet, since the light does not have to pass through any of the elements, as in the Fabry-Perot etalon. The task of producing such assemblages of plates to the required flatness and uniformity is so formidable that only a few have ever been made (all by Adam Hilger, Limited) and they are very expensive. Also, their use is not simple. [See W. E. Williams, *Nature*, **127**, 816 (1931) and *Proc. Phys. Soc. (London)*, **45**, 699 (1933)].

Lummer-Gehrcke Plate. The Lummer-Gehrcke Plate, developed in 1903,¹⁰ utilizes the interference between successive reflections in a thin plate, at nearly the critical angle of total reflection, as shown in Figure 17. The Lummer-Gehrcke Plate gives high resolution and a relatively bright interference pattern, but this advantage has become less important with the development of multilayer coatings for the Fabry-Perot etalon, so that the Lummer-Gehrcke Plate is now little used. (For details on its use see S. Tolansky, "High Resolution Spectroscopy," London, Methuen, 1947.)

The Echelle. The most recent high-dispersion device is the echelle, suggested by G. R. Harrison,¹¹ and produced successfully by Bausch & Lomb Optical Company. The

echelle can be considered an intermediate transition between a reflection echelon and a coarse plane grating. The Bausch & Lomb echelles typically have 200 grooves/inch, over an area of 3" × 6", and are blazed at about 63°. In use, the angle of reflectance is usually very nearly the same as the angle of incidence, so that 4500 Å, for example, will appear approximately in the 500th order. The free spectral range is then about 5–10 Å, so that a high dispersion spectrograph must be crossed with the echelle to separate the overlapping orders. An echelle can be treated as a very coarse grating, to compute dispersion, resolution and speed.

As a tool to record and analyze the complex spectra of the heavy elements—lanthanides (rare earths) or actinides (Th, U and transuranic elements)—the echelle has many practical advantages:

- (1) It can be produced commercially more readily than the echelon.
- (2) The lower order of interference, as compared to the etalon, echelon or Lummer plate, makes it possible to employ a compact 1.5–3 meter spectrograph as the cross dispersion element.
- (3) Therefore, the entire spectrum from 2000 Å–10,000 Å can be photographed on about 20" of spectrogram.
- (4) Wavelengths can readily be measured to thousandths of an Angstrom. Indeed, the limit of precision is usually set by the source, rather than the instrument.

Gratings at High Angles. If a grating is tilted to a high angle of 60–65°, so that reflections are obtained from the steep rather than the shallow side of the groove, the effect is much the same as that of the

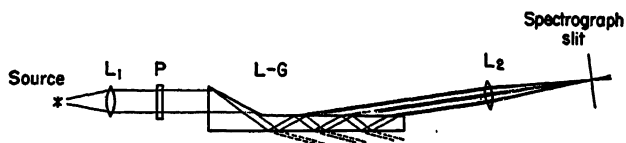
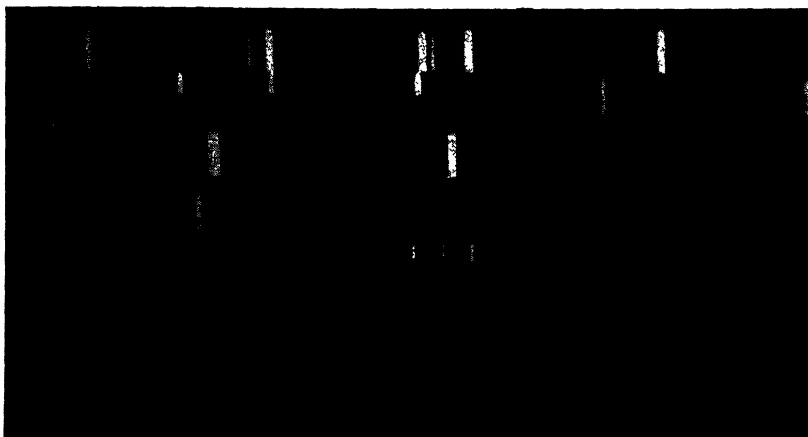


FIG. 17. Optical arrangement in the external mounting of the Lummer-Gehrcke plate. (From "Practical Spectroscopy," 1st Ed., G. R. Harrison, R. C. Lord, and J. R. Loofbourow, Prentice-Hall, Inc., 1948)



(Courtesy of Bausch & Lomb)

FIG. 18. Sorted ordergram.

echelle. Thus a grating of 7448 grooves/inch, used at 63° , will record the 24th order of 2537 Å or the 11th order of 5461 Å.

For a given wavelength, a grating so used will have the same resolution and linear dispersion as an echelle or echelon of comparable width used in the same focal length instrument. For, if W is the width, b the "ruling constant" (spacing) and n the order number, the resolution will be given by:

$$\frac{\lambda}{d\lambda} = Nn = N \cdot \frac{2b \sin i}{\lambda} = 2N \cdot \frac{W \sin i}{N \lambda} = \frac{2W \sin i}{\lambda}$$

Also, if f is the focal length, and r the angle of reflectance, the linear dispersion (equal to the angle of incidence in the mountings used) is given by:

$$\begin{aligned} \frac{d\lambda}{dl} &= \frac{d\lambda}{dr} \frac{dr}{dl} = \frac{b \cos r}{n} \cdot \frac{1}{f} = \frac{b \cos i}{n f} = \frac{W \cos i}{Nn f} \\ &= \frac{W}{2W \sin i / \lambda} \frac{\cos i}{f} = \cot i \frac{\lambda}{2f} \end{aligned}$$

Both expressions are independent of b and depend only on W , λ and i . This result is

so contrary to the normal conception that it is worth re-stating:

The resolution and dispersion of a grating or echelle for a particular wavelength are independent of the grooves/inch. The resolution is determined only by $W \sin i$, and the dispersion by $\cot i/2f$.

Relatively coarse gratings are preferable for high angle use, because they give more overlapping orders and thus fill in the spectrum. They also require an "order sorter" to separate the overlapping orders.¹² Since the free spectral range is relatively broad, the order sorter can be a low dispersion illuminator. A grating of 7500 grooves/inch used at $18-37^\circ$ may give a more useful dispersion for analytical work than a grating or echelle at higher angles, because the dispersion and resolution will not exceed the Doppler broadening of the lines in normal sources. A typical order-sorted spectrum is shown in Figure 18.

Illumination of the Spectrograph

The external condensing system employed to illuminate the spectrograph optics can markedly affect the spectra obtained. Several typical systems are illustrated in Figure 19. They may be divided into two basic types: (a) those that focus the source on the slit

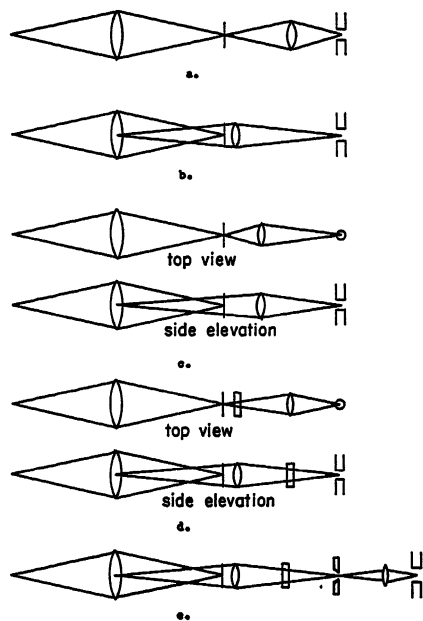


FIG. 19. Illuminating systems for spectrochemical analysis.

- (a) Source projected on slit.
- (b) Source projected on collimator.
- (c) Spherocylindrical lens projecting vertical line on slit and horizontal image on collimator.
- (d) Crossed cylindrical lenses projecting vertical line on slit and horizontal image on collimator.
- (e) System to select a portion of the source by projection on a diaphragm.

and (b) those that form an image of the source at the prism or grating.

An image formed on the slit of a stigmatic spectrograph will reproduce along each spectrum line the vertical variations in illuminance within the source for that particular wavelength. Therefore, such spectra may be employed to study the geometrical distribution of temperature or plasma conditions in various forms of spark, arc, flame or discharge tube. Because the spectral lines reproduce the source structure, they are not uniform and do not lend themselves to highly repeatable densitometer readings from sample to sample in routine quantitative spec-

trochemical analysis. Accordingly, system (a) Figure 19 is employed either to study source structure or as the simplest means of obtaining maximum speed.

For highly accurate quantitative spectrochemical analysis, particularly if a stepped filter or sector disk is to be employed to obtain directly the emulsion characteristic curve, it is desirable to obtain spectral lines uniform in density to within several per cent. To obtain such lines three conditions must be met by the condensing system: (1) The slit must be uniformly illuminated along its length. This is normally achieved merely by positioning the source sufficiently far from the slit. (2) All the light rays that pass through the desired slit height must pass through the vertical aperture of the spectrograph optics and play their part in forming the final spectral image. (3) The condensing system must not form a vertical image of the source anywhere near the slit or focal plane, since this would partially reproduce the source structure in the spectral lines. Conditions (2) and (3) are met by forming on the prism or grating an image of the source shorter vertically than the aperture. Typical condensing systems are:

(a) A single spherical lens at the slit, Figure 19b, projecting an image of the source on the dispersing element. This is used primarily in prism spectrographs or in grating instruments where the ruled area is square.

(b) A spherocylindrical lens placed a short distance ahead of the slit, Figure 19c, forming a line image of the source on the slit but a horizontal image of the source on the dispersing element. This fills a rectangular aperture better.

(c) Two crossed cylindrical lenses, Figure 19d, one as above forming a vertical line image of the source on the slit, the other at the slit projecting a horizontal bar image of the source at the grating. The second lens maintains the condition for line uniformity while the first fills the aperture horizontally, the combination transforming a source that

is normally taller than it is wide into an illuminated patch wider than it is tall, more nearly equal to the normal rectangular ruled area of a grating.

When it is desired to select a portion of the source image and yet obtain uniform lines, a lens or concave mirror is used to project an enlarged image on a diaphragm which is used to screen out the undesired sections, Figure 19e. An image of the diaphragm is then formed on the dispersing element by system cord.

REFERENCES

1. RAYLEIGH, LORD, "Wave Theory," Encyc. Britt., 9th ed., XXIV, 1888.
2. HARDY, A. C., PERRIN, F. H., "Principles of Optics," p. 411, McGraw-Hill Book Co., 1932.
3. HARRISON, LORD, AND LOOFBOUROW use a similar expression, but cancel out L on the assumption that the allowable slit height is always directly proportional to the focal length. Such an assumption is justified for similar optical arrangements, but may not hold for dissimilar designs. Then the system which permits the relatively taller slit is superior. See Harrison, Lord and Loofbourow, "Practical Spectroscopy," Prentice-Hall, 1948, pages 138 and 139.
4. HARTMANN, J., *Astrophys. J.*, **8**, 218 (1898).
5. SAWYER, R. A., "Experimental Spectroscopy," p. 229. Prentice-Hall, 1944.
6. ROWLAND, H. A., *Phil. Mag.*, **13**, 469 (1882); **16**, 197 and 210 (1883).
7. BEUTLER, H. G., *J. Opt. Soc. Am.*, **35**, 311 (1945).
8. SIRKS, J. L., *Astronomy and Astrophysics*, **13**, 763 (1894).
9. WADSWORTH, F. L. O., *Astrophys. J.*, **3**, 54-58 (1896).
10. LUMMER, O., AND GEHRCKE, E., *Ann. d. Physik.*, **10**, 457 (1903).
11. HARRISON, G. R., *J. Opt. Soc. Am.*, **39**, 522 (1949); HARRISON, G. R., AND BAUSCH, C. L., Proc. London Conf. Opt. Instruments (1946), John Wiley & Sons, Inc., New York (1947).
12. JARRELL, R. F., *J. Opt. Soc. Am.*, **45**, 259 (1955).

OPTICS—EFFECTS ON ACCURACY. See ACCURACY IN SPECTROCHEMICAL ANALYSIS, p. 99.

PHOTOGRAPHIC EMULSIONS: SPECTROSCOPIC PROPERTIES*

The object of a complete theory of photographic emulsions is to provide an explanation for the observed experimental facts and to make possible predictions about the behavior of any given emulsion under a given set of experimental conditions. Although this goal has not yet been reached, the recent development of a theory of thick emulsions^{1, 2} has brought us a long step closer to it. A brief outline of this theory and its results will be given here, with emphasis on the interpretation of physically measurable quantities. Before describing the theory, a few pertinent properties of an emulsion should be reviewed.

A photographic emulsion is comprised of a suspension of photosensitive silver halide crystals or grains in a (more or less) transparent layer of gelatine. When the emulsion is exposed to light, some of these silver halide grains acquire a so-called latent image and become reducible by developing agents. The final negative image consists of all these reduced silver grains, the unreduced silver halide grains having been removed by the fixing bath. Experimentally, it has been found that (with some exceptions) the weight of silver per unit area of the negative image is directly proportional to the optical density of the negative,¹⁰ showing that Beer's law holds for the reduced silver deposit. The plot of density against the log of exposure is known as the characteristic curve or the H and D curve of the emulsion. It has an approximate S shape, with a curved toe section, a more or less straight section in the middle, and a shoulder section at high densities. The slope of the straight line section is known as γ , and its extrapolated intercept at the log

* From Proc. Colloquium Spectr. Intern. VIII Special issue of *Chimica*, 1960, by permission.

exposure axis determines the H and D inertia i . At high exposure values density approaches the saturation density D_s as a limit if reversal is neglected. Since the development of a grain is an all-or-none process density is also proportional to the number of grains developed, and the ratio of density to saturation density is both the fraction of grains made developable by the exposure that produced the density in question, and the probability $\bar{P}(E)$ that an average grain in the exposed area will become developable after the exposure. Since any real emulsion absorbs an appreciable amount of light (the transmittance of the undeveloped SA 1 emulsion to green light for example is less than 0.5 %) the silver halide grains near the back surface of an emulsion receive far less light than do the grains near the front surface. This variation of light intensity throughout the emulsion as a result of absorption must be taken into account when the relationship between exposure and developability of grains in a thick emulsion is considered, and this is precisely the stumbling block that could not be handled previously. The problem can be solved, however, by starting with the relationship between exposure and developability of grains in a single-grainlayer emulsion and then suitably averaging this function over the thickness of the emulsion. In so doing we must take account of the manner in which the emulsion absorbs light, and it is natural to assume that this occurs according to Beer's law. Assuming Beer's law to hold, we shall use σ to designate the absorption cross section of a silver halide grain and its surrounding small volume of gelatine, and a to designate the absorption cross section of the silver grain formed from it upon development. The probability $P(E)$ that a grain of a single-grainlayer emulsion will become developable when subjected to an exposure E may be represented by a power series in kE where the constant k is proportional to the absorption cross section of a silver halide grain (without a contribu-

tion from gelatine, however, which enters into σ)

$$P(E) = \sum_{n=q}^{\infty} A_n (kE)^n \quad (1)$$

($q \geq 1$). Under the assumptions made, the average probability $\bar{P}(E)$ for the grains of an emulsion of thickness d becoming developable when the exposure at the surface of the emulsion is E is obtained from $P(E)$ simply by multiplying the terms in the n -th power of kE by the factor¹

$$F_n = \frac{1 - e^{-nN_0\sigma d}}{nN_0\sigma d} \quad (2)$$

(here N_0 is the number of grains per cubic centimeter of the emulsion). Further success of the theory now depends upon the manipulation of the resulting series. It will be easier to obtain useful results if the case of an infinitely thick emulsion, for which the exponentials vanish, is considered first. Using equations (1) and (2) and the definition of $\bar{P}(E)$ as D/D_s we obtain, after some algebraic manipulation, the following expression for the "natural density" $\ln(1/T)$ of an infinitely thick emulsion:

$$\ln\left(\frac{1}{T}\right) = \frac{a}{\sigma} \sum_{n=q}^{\infty} \frac{A_n}{n} (kE)^n. \quad (3)$$

Differentiating this with respect to $\ln(kE)$ gives:

$$\frac{d \ln(1/T)}{d \ln(kE)} = \frac{a}{\sigma} P(E). \quad (4)$$

The natural density of an emulsion of finite thickness d is a difference of two expressions of the form (3), and its slope is a difference of two terms of the form (4). Thus, if our assumptions are valid, $P(E)$ could be determined simply from measurements of the instantaneous slope of the H and D curve, without the necessity of grain counts on single-grainlayer emulsions. Since $P(E)$ approaches unity at large exposure values of E the limiting slope of an infinitely thick emulsion is:

$$\lim_{\ln(kE) \rightarrow \infty} \frac{d \ln(1/T)}{d \ln(kE)} = \frac{a}{\sigma} \quad (5)$$

The straight line section of an infinitely thick emulsion is asymptotic to equation (3). The equation of the asymptote is obtained by integrating equation (5) with respect to $\ln(kE)$. This gives

$$\ln\left(\frac{1}{T}\right) = \frac{a}{\sigma} \left[\ln E - \ln\left(\frac{C}{k}\right) \right] \quad (6)$$

where C is an integration constant which cannot be a function of k , σ or a . Equation (6) has the same form as the equation for the straight line section of the H and D curve,

$$D = \gamma(\log E - \log i). \quad (7)$$

If an emulsion is sufficiently thick it will have a straight line section whose slope, γ , will be a fair approximation to the slope of the infinitely thick emulsion, so that equations (5) and (6) may be applied to it. Equating the constant parameters in equations (6) and (7) we see that γ is equal to the ratio of the absorption cross sections of a developed silver grain and the silver halide grain (with the surrounding small volume of gelatine) from which it was formed, while inertia is inversely proportional to the absorption cross section of the silver halide grain (without the gelatine contribution). From this we may deduce that γ will increase with time of development owing to the increase in size of the developed silver grains, as measured by a , and will reach a limiting value when all developable grains have been fully reduced. At the same time, the inertia point will remain constant since the expression for it does not depend on development conditions. This behavior is actually observed in normal development in the absence of bromide. The presence of k and σ in equation (6) permits us to interpret variations of γ and inertia in terms of the absorption cross sections of silver halide grains and the absorptivity of gelatine. If other things are equal, a large value of k implies a large value

of σ , a low value of γ , and a low value of inertia, thus explaining the combination of low contrast and high sensitivity usually associated with coarse-grained emulsions. A large value of γ , on the other hand, implies a small value of σ , a small value of k , and a large value of inertia, and explains why fine-grained emulsions usually have high contrast and low sensitivity. The influence of gelatine on σ can cause an emulsion to have low contrast, however, even if the inertia is not low. Thus, the low contrast of unsensitized gelatine emulsions in the far ultraviolet is traced directly to the high absorbance of gelatine in that wavelength region, while the high contrast of several spectrochemical emulsions near their longwave sensitivity limit is correlated with high inertia values and low absorbance of gelatine in the visible and near ultraviolet regions. The variation of γ as a result of reciprocity failure cannot be explained under our initial assumptions, however, for it implies that, contrary to Beer's law, σ varies with the intensity of the exposing radiation. In order to account for the experimental observations it will be necessary to assume that σ is a function of the intensity of exposing radiation, passing through a maximum at the intensity corresponding to reciprocity optimum. Since we cannot assume that σ will vanish altogether, it must approach some limiting value both at very low and very high intensities. If this presumed variation of σ with intensity is due to the silver halide material and not to gelatine, k should pass through a maximum simultaneously with σ . Thus, lowest γ and lowest inertia should both be found at reciprocity optimum, where time and intensity scale gammas are equal. The Schwarzschild coefficient p , which is used for quantitative description of reciprocity failure, is in our view just a measure of the rate of change of σ with intensity. Since it is defined as a ratio of the slopes of time and intensity scale curves, the absorption cross section a of the developed silver grains cancels out

and p will be independent of development conditions if the intensity with which the time scale is produced is always taken from the same part of the intensity scale curve. When variable development times are concerned this condition is best expressed by requiring that the time scale be produced with an intensity capable of producing a definite *reduced density* D/D_s that must lie near the top of the straight line section of the intensity scale curve when the exposure time is the same as was used for producing the intensity scale curve. The high value of D/D_s is necessary to ensure that the values of p obtained are in accordance with the convention requiring p to be less than unity on the low intensity side of reciprocity optimum and greater than unity on the high intensity side of reciprocity optimum. Since σ must eventually approach a limit at very low and very high intensities its rate of change will have to decrease and finally vanish at very low and very high intensities, requiring p to approach unity again. There is some experimental evidence that this actually happens^{4, 5} to p . The predicted variation of inertia has also been observed¹¹ for a number of spectroscopic emulsions. Since all of these conclusions on reciprocity failure follow from the assumption that Beer's law does not hold for the undeveloped emulsion, a measurement of the manner in which the transmittance of an emulsion varies with intensity is of critical importance for determining the reciprocity failure characteristics of an emulsion. Measurements at different intensity levels are not available at present, even though the experiments of Bloch and Renwick⁶ had shown already in 1916 that Beer's law is not obeyed by undeveloped emulsions. Apparently no one connected this with reciprocity failure and their work does not seem to have been followed up.

For the results obtained up to this point the functional form of $P(E)$ has been of no importance as long as it possessed proper limiting behavior. When assumptions are

made concerning the form of $P(E)$ some further very important conclusions may be drawn concerning the behavior of the Baker-Sampson (Seidel) and Kaiser functions.^{3, 9, 12} Thus, if we are dealing with an emulsion consisting of uniformly sensitive grains and the reverse primary process can be neglected, $P(E)$ will be given by the Poisson distribution of exposure,

$$P(E) = \sum_{n=q}^{n=\infty} (-1)^{n+q} \binom{n-1}{q-1} \frac{(kE)^n}{n!} \quad (8)$$

where q is the minimum number of quanta required to make a grain developable. Algebraic manipulation of equation (3) and a few approximations then show that a function of the form

$$q \frac{\sigma}{a} \ln(1/T) + \ln(1-T) \quad (9)$$

should be very nearly linear function of $\ln E$, with slope q . When natural logs are replaced by common logs, this is just a variant of the Kaiser function, written in the form used by Candler:⁷

$$\Delta = \Phi D + \log(1-T). \quad (10)$$

Since a/σ was identified with γ , the transformation constant Φ is just equal to q/γ . It is interesting to note that the slope of this form of the Kaiser function remains fairly independent of wavelength, even if γ varies, as Candler has shown.^{7, 8} For a number of spectroscopic emulsions Candler found slopes close to (although not exactly) two. If development of these emulsions is controlled to give a gamma around two the transformation constant Φ in equation (10) is nearly unity and the whole expression becomes equal to the Baker-Sampson (Seidel) function. Under these conditions the Baker-Sampson (Seidel) function will be as effective in linearizing the characteristic curve as the Kaiser function is.

Conclusions

The interpretation of the parameters of the H and D curve and the Kaiser function

given by our theory permits one to form an intelligent understanding of what may or may not be expected of a photographic emulsion. The multiple connections between the different parameters and the physical properties of the emulsion correlate and explain a number of previously unrelated empirical facts and establish a foundation for a complete theory of photographic emulsions.

REFERENCES

1. ARRAK, A., *Appl. Spectroscopy*, **12**, 171 (1958).
2. ARRAK, A., *Appl. Spectroscopy*, **13**, 143 (1959).
3. BAKER, E. A., *Proc. Soc. Edin.*, **45**, 166 (1925), **47**, 34 (1927), **48**, 106 (1928).
4. BAKER, E. A., *J. Phot. Sci.*, **4**, 101 (1956).
5. BAKER, E. A., personal communication.
6. BLOCH, O. AND RENWICK, F. F., *Phot. J.* **56**, 49 (1916).
7. CANDLER, C., *Spectrochim. Acta*, **8**, 262 (1956).
8. CANDLER, C., *Appl. Spectroscopy*, **13**, 97 (1959).
9. KAISER, H., *Spectrochim. Acta*, **3**, 159 (1948).
10. MEES, C. E. K., *Theory of the Photographic Process*, Macmillan, New York 1942, p. 226-32.
11. *Ibid.*, table 68, p. 707.
12. SAMPSON, R. A., *Mon. Not. Roy. Astronom. Soc.*, **85**, 212 (1925).

ARNO ARRAK

PHOTOGRAPHIC SPECTROGRAPHS

Since the earliest days of spectroscopy, spectrographs have been employed to record photographically a permanent record of a spectrum under investigation. Among the advantages of such a spectrogram are:

(a) The simultaneous recording of all lines, at high resolution and in an exposure usually of seconds.

(b) A permanent record, not only of the lines which are specifically sought but also of lines from all other elements present in significant amounts. Thus old plates may be checked for the presence of lines not originally suspected or detected.

(c) The ability, by measuring the relative spacing of unknown and standard lines, to determine wavelengths out to .001 Å.

Despite the advent of multiplier phototubes, thermopiles and various other photodetectors, and the availability of high-speed and extremely sensitive recorder and other read-out systems, the fundamental advantages of the photograph assure the spectrograph a continued and widespread use. Spectrographs have been employed industrially for emission spectrochemical analysis. As scientific tools they have been used to measure the wavelengths of electronic transitions in all the elements, thus defining the electronic configuration. Study of the emission or absorption spectra of molecular band systems has revealed vibrational and rotational frequencies of the molecule. A comparison of the relative intensities of various lines permits a determination of the temperature of a gaseous system.

This article describes spectrographs with coverage in the region 2000 to 12,000 Å. Spectrographs for the region below 2000 Å are described in the article on Vacuum Spectroscopy. Concave grating and plane grating instruments are discussed on pages 179-188.

Prism Spectrographs

Fixed Position "Small" or "Medium" Quartz Spectrographs. To photograph in a single exposure the entire wavelength range from approximately 2000 Å to 8000 Å or 10,000 Å, the most common instrument is the small or medium quartz spectrograph. Unfortunately, while quartz is a highly useful optical material, since it has high transparency and dispersion in the important far ultraviolet (2000 Å-3000 Å), it has the unfortunate disadvantage of double refraction and circular polarization. While double refraction does not introduce serious aberrations in the image so long as the crystal is cut so that its optical axis is in a principal plane and parallel to the prism base, the circular polarization may produce a doubling of the image unless the prism is constructed according to Cornu, of identical 30°-60°

components adhered together. One component is dextrorotatory, the other levorotatory; similarly, the collimator lens may be dextrorotatory, the camera lens levorotatory. Such a symmetrical arrangement eliminates the doubling of the slit image which would otherwise occur.

The construction indicated in Fig. 1 is typical. The plate is inclined at almost 30° to the central ray, because there is no point in attempting to achromatize the system and the focal length at 2000 Å is so much shorter than at 10,000 Å. This tilt has the advantage of almost doubling the linear dispersion, although at the same time it broadens the line image. Because wholly uncorrected systems may have such a curvature of the focal field as to fracture glass plates bent to the required curve, two-element or aspherical camera lenses have been employed to produce a "flat field".

Much of the early work in spectrochemical analysis, of non-ferrous alloys particularly, was performed on small quartz spectrographs, focal length for sodium D about 20 cm, plate size $3\frac{1}{4}" \times 4"$, or on medium spectrographs, focal length about 60 cm, plate size $4" \times 10"$. Adam Hilger, Ltd., Bausch & Lomb, Gaertner, Zeiss, Belling-

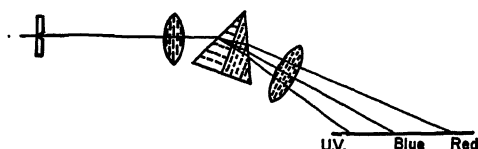


FIG. 1. Optical path of a typical small or medium quartz spectrograph.



FIG. 2. A large Littrow quartz spectrograph. To focus for a lower wavelength setting, it is necessary to make the three adjustments indicated by the arrows.

ham & Stanley, Jobin & Yvon have been the most important manufacturers.

Medium Glass Spectrographs. These are similar in construction to the medium quartz, except for a simple flint "uvio" prism (transmitting the near ultraviolet to about 2800 Å); they were developed by Adam Hilger, Ltd., to increase the dispersion and resolution at the higher wavelengths, where the dispersive power of quartz becomes really poor.

Littrow Quartz or Glass Spectrographs. The Littrow mounting of a prism (Fig. 2) utilizes far less optical material than a system using a Cornu prism, and so is very widely used for applications requiring high dispersion and resolution, to reduce the cost of the quartz or glass alone. The back surface of the prism is silvered or aluminized. In this case, a single lens and simple 30° prism is sufficient, even for such doubly refracting and birefringent materials as quartz, since effects of double refraction or polarization introduced to the entrant beam are cancelled out by the emergent beam.

A typical large Littrow quartz spectrograph, suitable for photographing ferrous or similarly complex spectra, will have a focal length of 1.7 to 1.8 meters and will require two or three different settings of a $10"$ plateholder to cover the wavelength range from 2000 Å to 8000 Å. Accordingly, adjustments must be provided to change wavelengths. This means that it is necessary to:

- rotate the prism to bring the desired wavelength range on the plate,
- move the prism and lens along the instrument axis to compensate for the change in focal length of the lens, and
- tilt the plate to compensate for the variation in difference of focal length for the extreme rays.

In the earliest Littrow spectrographs (Adam Hilger, Gaertner Scientific) these three adjustments were made by three independent controls. In 1929 Bausch & Lomb introduced an instrument in which the

prism and lens were moved axially along the instrument by a steel tape, while for ten different settings the prism table was rotated by a spring against ten adjustable screw stops. Plate tilt settings to correspond were still made independently.

Adam Hilger, Ltd., in 1936 developed a fully automatic Littrow spectrograph, utilizing a screw drive to move the prism and lens, with a cam to define the prism rotation and a second cam to set the plateholder tilt. A drum secured to the screw was calibrated to read wavelengths directly.

Glass prisms and lenses are employed in Littrow spectrographs interchangeably with the quartz, to produce higher dispersion and resolution in the range above 3600 Å.

The advantages of the Littrow prism mounting are compactness, simplicity of optics, and good dispersion and resolution in the range 2500–3500 Å, where the spectra of metals are most complex. Scattered light resulting from reflections from the front face of the lens can present a major problem, only partially alleviated by putting a mask across the middle of the lens or by tilting the lens a slight amount vertically. The dispersion at high wavelengths may be inadequate.

Gaertner Large Quartz Spectrograph.

To avoid the scattered light of the Littrow system, Gaertner¹ developed a spectrograph employing a Cornu prism, a mirror to reflect the light back parallel to the entrant beam, and a separate camera lens (Fig. 3). This spectrograph also pioneered in using a 14" camera for wider wavelength coverage. It represented the most advanced optical design in prism instruments achieved in the United States.

Multiple Prism Spectrographs. Because large quartz prisms require both rare and expensive natural crystals, or very special and expensive fused quartz, it is far less expensive to obtain increased dispersion and resolution in a prism spectrograph by utilizing a train of multiple prisms. Zeiss and Steinheil have pioneered in such instruments.

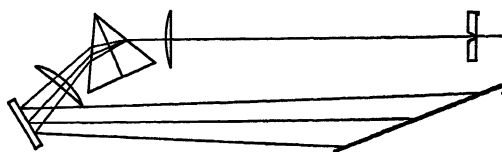


FIG. 3. Optical path of Gaertner two-lens large-quartz spectrograph.

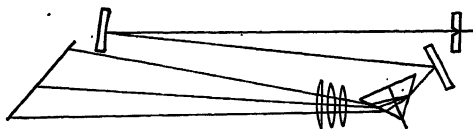


FIG. 4. Jobin & Yvon large quartz spectrograph.

Several cameras are offered. A long focal length, low aperture camera is supplied for spectrochemical analysis, whereas a short focal length, high aperture camera will be used for Raman or similar work. These two instruments seem best suited to research applications.

Jobin & Yvon and Société Générale d'Optique (Huet) in France have developed large, fixed position quartz spectrographs with focal lengths up to 3 meters and plate-holders up to 54 cms in length, covering an extended wavelength range at dispersions almost double the standard large Littrow. The Jobin & Yvon instrument employs a concave mirror as collimator, and a triple aplanat camera lens to produce a flat field (Fig. 4). The mounting is vertical so that the slit axis and plateholder are horizontal. These spectrographs are particularly designed for industrial use.

In West Berlin, Fuess manufactures what is probably the most advanced prism spectrograph designed up to the date of this article. It uses four fused quartz prisms to produce a high dispersion in a compact arrangement (Fig. 5). This is the only prism spectrograph which the author has seen with working resolution adequate to separate the .07 Å doublet of the iron triplet at 3100 Å, requiring a resolution of 44,000.

Féry Spectrograph. In the Féry mount-

ing (Fig. 6) manufactured commercially by C. Beaudoin in France, cylindrical surfaces on the front and rear faces of a single quartz prism act as lenses, so that there is only the one optical element. As contrasted to all other prism spectrographs, the spectral lines from a Féry mounting are straight, but astigmatic.

High Aperture Prism Spectrographs.

For Raman studies and for other work involving low light levels, several manufacturers produce prism spectrographs of generally conventional design but with high aperture ratios (Fig. 7). Perhaps the simplest is the Hilger & Watts F/4 Raman Spectrograph, which has a collimator of 60 cm focal length and a camera of 20 cm focal length, both 5.1 cm in diameter. The instrument has interchangeable quartz and glass optics. Hilger & Watts manufactures also a large two prism glass spectrograph with interchangeable cameras of F/1.5 and F/5.7.

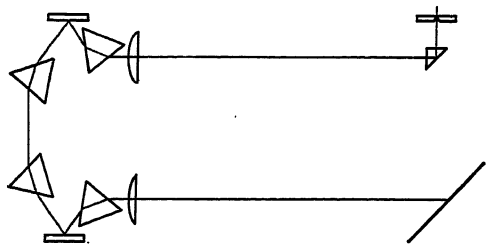


FIG. 5. The Fuess four prism quartz spectrograph. The prisms and the plateholder are rotated by individual cams to change wavelength range.

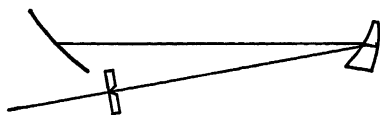


FIG. 6. The Féry quartz spectrograph.

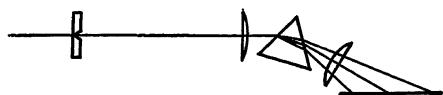


FIG. 7. Typical design of a high aperture spectrograph, where the focal length of the camera lens is much shorter than that of the collimator.

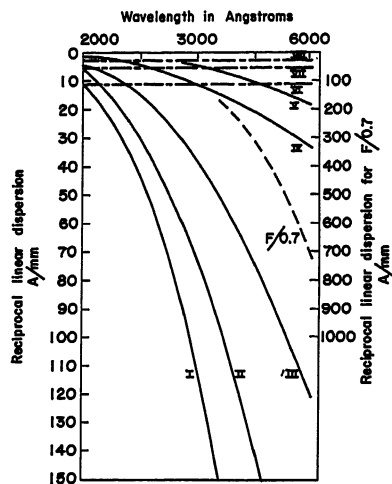


FIG. 8. Dispersion curves for typical prism and grating spectrographs.

- I. "small quartz"
- II. F/3.5 three prism quartz
- III. "medium" quartz
- IV. large Littrow quartz
- V. large Littrow glass
- VI. 1.5 meter grating, 15,000 grooves/inch
- VII. 3.4 meter grating, 15,000 grooves/inch
- VIII. 3.4 meter grating, 30,000 grooves/inch
- F/0.7 glass prism (use right-hand scale)

TABLE 1. RECIPROCAL LINEAR DISPERSION OF TYPICAL PRISM SPECTROGRAPH, A/MM

Wavelengths, A	2300	2700	3100	3700	4500	6000
Small Quartz	18	31	47	87	162	360
Medium Quartz	6.1	10.4	15.6	29	54	120
Large Quartz Lit-trow	1.9	3.3	5.1	8.1	15	33
Large Glass Littrow				3.2	6.7	18
Three Prism Quartz, F/3.5	11	22	36	59	100	300
F/0.7 Glass					190	700

In France, Société Générale d'Optique specializes in high aperture quartz and glass prism spectrographs. These include an F/0.7 glass spectrograph and a highly corrected three prism F/3.5 quartz spectrograph capable of resolving the Fe 3100 A triplet at a dispersion of 36 A/mm.

Dispersion curves for typical prism spec-

trographs are shown in Fig. 8. The data used for these curves are presented in Table 1.

REFERENCE

1. JACOBSON, S., J.O.S.A., **31**, 604 (T), (1941); **32**, 164 (1942).

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PHOTOMETRY—EFFECTS ON ACCURACY. See **ACCURACY IN SPECTROCHEMICAL ANALYSIS**, p. 99.

PRECISE OBSERVATION AND EMPIRICAL CLASSIFICATION*: HISTORY

More than two centuries elapsed between Newton's observation of the dispersion of white light by a prism, in the year 1666, and the achievement of any notable success in the interpretation of spectral regularities. Early in the nineteenth century Wollaston and Fraunhofer discovered independently the dark lines superposed on the continuum of the solar spectrum. In 1860 Foucault observed that the bright yellow lines characteristic of a sodium flame changed to dark lines on a bright background when the flame was placed between a brilliant arc and the slit of a spectroscope. He also noticed that these lines were in the same position as the D-lines of the solar spectrum. This marked the beginning of identification of elements in the sun and other celestial sources. At about the same time, Kirchhoff announced the laws governing absorption and emission of radiation that bear his name. These laws provided an explanation of the reversal of spectral lines and, in a sense, marked the beginning of astrophysics.

Angstrom's first detailed solar map is now only of historical interest, but is remembered on account of the introduction of the unit of wavelength.

The real beginning of precision spectroscopy is identified with Rowland's develop-

ment of a machine for ruling diffraction gratings of satisfactory optical quality. This program was first reported in 1882. Rowland's gratings found their way to leading universities and research centers in the United States and in Europe and figured in most of the important spectroscopic investigations during the next half century. The precision of wavelength measurement attainable by use of these gratings made possible the discovery and formal representation of numerical regularities in spectra. Rowland published a map of the solar spectrum covering the entire region then accessible to photography. In many respects the spectrograms that were incorporated into this work have never been surpassed. Rowland also set up a system of wavelength standards based on the law of superposition of grating orders. This law may be briefly stated as follows: Spectral lines of various grating orders are coincident in position when the products of the wavelengths by the respective order numbers are equal. For example, the third order of 4000 Å is coincident with the second order of 6000 Å or the first order of 12000 Å. Rowland's standards provided the basis for wavelength measurement until superseded by the system of international standards based on interferometric determinations initiated by Fabry and his associates just after the turn of the century. These, in turn, had followed and were dependent upon Michelson's evaluation of the length of the standard meter in terms of the equivalent number of wavelengths of the red cadmium line.

As soon as precise methods of observing spectra became possible, following the introduction of the Rowland gratings, a large amount of spectral data were accumulated, that originated mostly in the source elements that are placed in the first two columns of the periodic table. This work is associated mainly with the names of Kayser and Runge in Germany, and with that of Rydberg in Sweden. As might have been expected, atomic hydrogen, which possesses

* The second in a consecutively developed series of articles on fundamentals of Optical Emission Spectra: see *Introduction: Designation and Description of Spectra for list of topics*, p. 202.

the simplest spectrum of all the elements, and which is conspicuous in stellar spectra of certain types, was the first for which the wavelengths of the visible lines could be related by a simple formula. This was accomplished by Balmer in 1885. The original formulation was

$$\lambda = h \frac{n_2^2}{n_2^2 - n_1^2}$$

in which $h = 3645.6 \text{ \AA}$, $n_1 = 2$, and $n_2 = 3, 4, 5, 6 \dots$ for the series starting in the visible red region with $\lambda = 6562 \text{ \AA}$, known as H_α . Later in the hands of Rydberg and Ritz the formula was changed into the following equivalent form to give the wave numbers of the series members:

$$\nu = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \text{ where } n_2 = 2, 3, 4 \dots$$

This formula, which was in accord with the more general series formulas developed in the same period, will be given more extended discussion.

The spectra of the alkalis and of the alkaline earths, which are comparatively simple, show obvious regularities consisting of long series of doublets in the instance of the former and of triplets in the instance of the latter. Similarly conspicuous triplet series are characteristic of the spectra of zinc, cadmium, and mercury. No satisfactory formula for representing these series was found until the wavelengths were converted to wave numbers. The first successful formula, applied in the first instance to the alkali spectra, was discovered by Rydberg. It is of the form

$$\nu_n = \nu_\infty - \frac{R}{(n + \mu)^2}$$

According to this expression, the wave number of a spectral line in the series is equal to the difference of two terms. The first term is the wave number of the limit of the series. This is apparent since n represents a series of increasing integers. As n increases, the sec-

ond or running term goes to zero. When n takes its starting or smallest value, the value of ν_n is that of the first line of the series. The letter R is used to designate the Rydberg constant. Strictly speaking, this is not a constant, but is a quantity that varies by a small amount from atom to atom, increasing with increasing atomic number, but approaching a constant. Since the interpretation of this quantity is an important feature of the early development of atomic theory, further discussion is reserved for that section. The letter μ in the denominator of the running term was used to designate a numerical correction to n . It is characteristic of the particular series and in general not a whole number. Four series were found in these simple spectra. Various names were given these series, but the following, based partly on the physical characteristics of the lines, are generally used: principal, sharp, diffuse, and fundamental. Each series is characterized by its own limiting term and correction constant in the denominator of the running term. Interrelationships were found among the various series that indicated that the first or limiting term had the same general form as the running term. These relationships are known as the Rydberg-Schuster and Runge laws and are included in the following formulas representing the four series:

Principal series

$$\nu_n^p = \frac{R}{(1 + S)^2} - \frac{R}{(n + P)^2},$$

$$n = 1, 2, 3, \dots$$

Sharp series

$$\nu_n^s = \frac{R}{(1 + P)^2} - \frac{R}{(n + S)^2},$$

$$n = 2, 3, 4, \dots$$

Diffuse series

$$\nu_n^d = \frac{R}{(1 + P)^2} - \frac{R}{(n + D)^2},$$

$$n = 2, 3, 4, \dots$$

Fundamental

$$\nu'_n = \frac{R}{(2 + D)^2} - \frac{R}{(n + F)^2},$$

$$n = 3, 4, 5, \dots$$

For characterizing spectral lines these same formulas were written in a shorthand notation of which the following is typical:

$$1S - nP$$

$$1P - nS$$

$$1P - nD$$

$$2D - nF$$

The coefficients are the integral parts of the Rydberg denominators associated with the particular transitions represented. This same notation with appropriate extensions has survived in the system now in use.

When the members of a series were made up of two or more components, each component was treated as forming its own series and an appropriate notation was introduced to cover these cases. An interesting feature of a sharp series is that the running term is always single. Hence all members show the same doublet or triplet separations (in wave numbers) as the limiting term.

The various possibilities of representation of actual frequencies by differences between terms, as illustrated by the Rydberg-Schuster and Runge laws, are included in a broader generalization known as the Ritz combination principle. It permits the prediction of many lines not included in the usual series. If we represent the Rydberg equation in somewhat more general form,

$$\nu = \frac{R}{(n_1 + \mu_1)^2} - \frac{R}{(n_2 + \mu_2)^2}$$

new series or new combinations are predicted when n_1 is made larger than in the limit of the usual series. Many such combination lines are observed.

Analysis of the spectra of a considerable number of elements in the categories noted was accomplished just after the turn of the

century. Most of the series could be represented by a Rydberg formula. Essentially all the results of these analyses are contained in two publications, "A Report on Series in Line Spectra," by Fowler,¹ and "Seriengesetze der Linienspektren," by Paschen and Götze.² The latter also contains the essential features of the analysis of the neon spectrum by Paschen,³ a classic work marking the first success in the interpretation of a new class of spectra.

The Rydberg formula is to be regarded as an approximation, relatively precise in the instance of series in the spectra of many elements. Assuming R to be a general constant, it is a two-constant formula permitting an entire series to be predicted where two members have been observed. Even when the formula is inadequate to represent series precisely, it is of considerable help in locating unidentified members among spectral data. An extensive table has been prepared by the Departments of Physics and Astronomy at Princeton University of the values of the function $R/(n + \mu)^2$ for the entire range of expected values of the denominator.

For more precise representation of series, formulas using more constants in the denominator of the expression for the term have been developed by Hicks and by Ritz. Two forms of the Ritz equation have been found most generally useful:

$$\nu_n = T_1 - \frac{R}{\left(n + a + \frac{b}{n^2}\right)^2}$$

and

$$T_n = \frac{R}{(n + a + bT_n)^2}$$

It is to be noted that in the second expression the running term itself is included as a correction in the denominator. More elaborate formulations extend the denominators into a longer power series.

These formulations are empirical, but subsequent developments demonstrate that

their authors displayed remarkable intuition, because the term structure of spectra is now firmly established and the detailed features of the formulas in general have a physical justification.

The formula for representing hydrogen spectra may also be considered as a special modification of the Rydberg formula. If the corrections, designated μ , to the denominators in the general form of the Rydberg equation become zero, the equation reduces to

$$\nu_n = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

This is the general series equation for hydrogen.

When n_1 is taken as 2 we obtain the Rydberg formula for Balmer's series. In accordance with the Ritz combination principle, other series are found, when n_1 is taken as 1, or other integers. In each instance n_2 begins with an integer larger by one than n_1 .

The series are named in each instance for the discoverer. Following are the names, together with the values of n_1 , from which the complete formulas may be constructed:

Lyman series:	$n_1 = 1$
Balmer series:	$n_1 = 2$
Paschen series:	$n_1 = 3$
Brackett series:	$n_1 = 4$
Pfund series:	$n_1 = 5$
Humphreys series:	$n_1 = 6$

The values of the wave numbers may be calculated from the Rydberg constant for hydrogen and the values of n_1 and n_2 . The Lyman series is completely in the extreme ultraviolet, the first line being at 1215 Å. The last four are all in the infrared. The first five series have been known for many years, but the last was not found until 1952.⁴ The first line of this series and the only one so far observed is at approximately 125,000 Å.

The theoretical interpretation of the hydrogen formula represented the beginning of the development of atom mechanics and the quantum theory of spectra.

While it is intended to call attention to

currently held views regarding the origin of spectra in accordance with accepted theories of atomic structure and to point out the physical basis of the modes of representation of spectral features, no detailed development will be attempted. A large selection of reference books is available that present the material in varying amounts of detail and with special emphasis on particular topics. The classic work is "Atombau und Spektrallinien" by A. Sommerfeld,⁵ the indexed reference being to the latest English edition. The following books are concerned entirely with atomic spectra and contain an extensive and detailed treatment of the theory: "The Structure of Line Spectra," by Pauling and Goudsmit⁶; "Introduction to Atomic Spectra" by White⁷; and "Atomic Structure and Atomic Spectra" by Herzberg.⁸ Important sections dealing with atomic emission spectra are to be found in "Atoms, Molecules, and Quanta," by Ruark and Urey,⁹ and in "Introduction to Modern Physics," by Richtmyer and Kennard.¹⁰ A summary account of spectral features and spectral notation, together with tables useful in analysis, and descriptions of representative spectra is included in the "American Institute of Physics Handbook,"¹¹ this particular section having been prepared by Dieke. "Theory of Atomic Spectra," by Condon and Shortley¹² is a rigorous presentation going beyond the scope of the other references. Frequent reference will be made to "Atomic Energy Levels, by Moore,"¹³ a compilation of the known levels of all spectra observed and analyzed.

A more recent treatise that includes a discussion of atomic spectra is "Atomic Physics" by Finkelburg.¹⁴

Professor Bengt Edlén of the University of Lund has prepared a comprehensive and detailed volume on "Atomic Emission Spectra" for the Springer Encyclopedia, now in press. It is expected that Edlén's modern and readable treatment of the subject, appearing many years after any of the listed general references, will find widespread acceptance.

REFERENCES

1. FOWLER, A., "Report on Series in Line Spectra," Fleetway Press, London (1922).
2. PASCHEN, F., AND GÖTZE, R., "Serien-gesetze der Linienspektren," Julius Springer, Berlin (1922).
3. PASCHEN, F., *Ann. Physik*, **59**, 297 (1919).
4. HUMPHREYS, CURTIS J., *J. Research NBS*, **50**, 1 (1953).
5. SOMMERFELD, A., "Atomic Structure and Spectral Lines" (English Translation of the Fifth German Edition) Methusen, London (1934).
6. PAULING, L., AND Goudsmit, S., "The Structure of Line Spectra," McGraw-Hill, New York (1930).
7. WHITE, H. E., "Introduction to Atomic Spectra," McGraw-Hill, New York (1934).
8. HERZBERG, G., "Atomic Spectra and Atomic Structure," Dover Publications, New York (1944).
9. RUARK, A. E., AND UREY, H. C., "Atoms, Molecules, and Quanta," McGraw-Hill, New York (1930).
10. RICHTMYER, F. K., AND KENNARD, E. H., "Introduction to Modern Physics," McGraw-Hill, New York (1955).
11. "American Institute of Physics Handbook," McGraw-Hill, New York (1957).
12. CONDON, E. U., AND SHORTLEY, G. H., "The Theory of Atomic Spectra," Cambridge University Press, New York (1953).
13. MOORE, CHARLOTTE E., "Atomic Energy Levels," Circular of the National Bureau of Standards 467, U. S. Government Printing Office, Washington, Vol. I (1949), Vol. II (1952), Vol. III (1958).
14. WOLFGANG FINKELNBURG, "Atomic Physics," McGraw-Hill, New York, 1950.

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RARE EARTHS MICROANALYSES

This article outlines the chemical isolation and spectrographic determination of small quantities (100 micrograms or less) of rare earths. The need for such analyses may arise either because the concentration of the rare earths in the sample is low, or because the sample itself is small. Rare earths affect the properties of many metals, ceramics, phosphors, semiconductors and electronic parts, and must often be determined at microgram

or sub-microgram levels. Samarium, europium, gadolinium and dysprosium strongly absorb thermal neutrons. All nuclear fuels, construction materials and auxiliary devices used in a nuclear reactor must therefore be checked to make sure that the concentration of these rare earths does not exceed a few tenths of a part per million. Small concentrations of rare earths are also of interest in mineralogical, geochemical, botanical and biochemical studies.

Rare earths are among the most abundant products of the fission of uranium and plutonium nuclei. They must be determined at various stages in the processing of spent nuclear fuels. Since fission product rare earths are extremely radioactive, the total sample size must be kept small, and appropriately sensitive procedures are needed.

Spectrographic methods are widely used for this type of analysis. Sample preparation technique depends on the size and gross composition of the sample, and on the degree of sameness of samples. If the concentration level of the element determined is high enough, if no spectral line interferences exist, and if a large number of similar samples are to be analyzed, no chemical pretreatment is necessary. The sample is finely ground together with suitable diluents and internal standards, and exposed by D.C. arc techniques.^{12, 13, 14}

If rare earth concentrations are low, however, and/or spectral lines of the matrix components interfere with rare earth lines, and/or samples are variable in gross composition or size, the rare earth group must be chemically isolated and concentrated. Typical methods are listed below under two categories: Carrier-free and Carrier methods.

Chemical Concentration of Rare Earths

Carrier-free procedures produce an undiluted sample and permit the greatest absolute sensitivity of detection. Unless monitored with radioactive tracers, however, these procedures must be performed very

carefully to avoid losses. Carrier methods are somewhat inferior in absolute sensitivity, but are not subject to error from losses during isolation.

Carrier-Free Methods. (1) *Thenoyl-trifluoroacetone (TTA)*.¹ Quantitatively extracts rare earths from aqueous solutions of pH > 4. Can be used to isolate rare earths from a large number of other elements by performing an extraction at pH 1, discarding the organic layer, raising the pH of the aqueous to 4.5, extracting rare earths, discarding the aqueous, and stripping the TTA layer with 1-1 HCl.

(2) *Cellulose pulp*.² Filter paper pulp which has been soaked in an ether-HNO₃ mixture will adsorb rare earths from a sample dissolved in this mixture. Since the pulp does not adsorb Th or U from this solution, micrograms (or milligrams) of rare earths can quickly be separated from grams of Th or U by this procedure. The rare earths are stripped from the pulp with HNO₃ at pH 2. The few micrograms of residual Th or U which may accompany these rare earths may be removed by repeating this procedure, or by TTA extraction.

(3) *Cupferron*.³ If the major constituent does not form an insoluble cupferrate, the rare earth cupferrate may be formed in an aqueous medium, extracted into chloroform, and recovered by alkali stripping or by evaporation and wet-ashing.

(4) *Removal of major constituent*: (a) By electrolysis: Ferrous alloys, etc., may be electrolyzed into a mercury cathode. The rare earths, which remain in solution may be concentrated and purified by TTA extraction. (b) By liquid-liquid extraction: In 6*M* HCl solution, uranium, zirconium and/or iron may be extracted away from rare earths with tri-*n*-octylamine.⁴ Thorium may be extracted from aqueous media at pH 1.0 with TTA,⁵ leaving rare earths in the aqueous layer. (c) By ion-exchange: Thorium⁶ and plutonium⁷ can be adsorbed from 8*M* HNO₃ solution by strongly basic anion exchange

resins; uranium⁷ is similarly adsorbed from 6*N* HCl solution, and Zr from 0.1*N* H₂SO₄ solution.⁸ In all cases, the rare earths are not adsorbed. Alternatively, zirconium may be passed through a cation column as the anionic fluoride complex, while the rare earths are retained.⁹

Carrier Methods. These are essentially precipitation methods, though other techniques may be used to aid in purification of the product. In carrier methods, a small quantity (usually 10–50 mg) of some pure rare earth (or chemically similar) compound is added to the sample, and the desired rare earths co-precipitated with it. This “carrier” facilitates handling of microgram amounts of rare earths, and usually serves as the matrix for the spectrographic exposure. Collection and transfer losses are compensated by measuring the ratio of the intensities of subject element lines to minor lines of the carrier. The element chosen as carrier must be free of the elements sought. The total quantity of the carrier element (if any) present in the original sample must be negligible compared to the quantity added as carrier. Yttrium is often used for this purpose, since pure material can be obtained at a relatively low price, and the yttrium spectrum is a simple one.

With yttrium or some true rare earth as carrier, microgram quantities of rare earths can be collected as hydroxides, fluorides, oxalates or cupferrates. These precipitating reagents are not specific for rare earths, however. The precipitate to be used in a given case must therefore be chosen so as to avoid precipitation of any undesired elements which may be present.

By the same token, the carrier element need not be a rare earth. Any element which precipitates under the same conditions as rare earths may be useful as a carrier for rare earths. For example, thorium can be used to co-precipitate rare earths from an acid solution of steel and other metals as the oxalate and/or fluoride.¹⁵

Spectrographic Determination

Carrier-Free Samples (100 μg rare earths or less). The best absolute spectrographic sensitivity for rare earths is obtained by evaporating a chloride solution of the pure rare earth fraction on the end of a pair of copper rods and exciting the dried residue with a 940 volt 4 μfd , 100 μH spark discharge.⁶ Absolute sensitivities for the detection of individual rare earths by this method are shown in Table 1.

When the total amount of residue is small, changes in the proportions of major components may cause a shift in the analytical curve of one or more of the components. Little information is available on this point in the case of the copper spark technique.

If a nitrate residue is evaporated on graphite, the influence of one rare earth on the analytical curve of another is essentially eliminated by the addition of 30 μg of Zn.² Sensitivity limits are then not as low as those listed for the copper spark, however. Different excitation sources were used in the two

cases, so that sensitivity figures may not be comparable.

Carrier Samples. If the trace rare earths are precipitated with a carrier (e.g. yttrium), the precipitate is usually ignited, mixed with graphite and exposed by the D.C. arc. Typical absolute sensitivities for this method are given in Table 1, assuming the burning of a 10-mg sample Y_2O_3 .

REFERENCES

1. BRONAUGH, H. J., AND SUTTLE, J. F., U. S. Atomic Energy Commission Report LA-1561 (1953).
2. FELDMAN, C., AND ELLENBURG, J. Y., *Anal. Chem.*, **30**, 418 (1959).
3. POPOV, A. I., AND WENDTLANDT, W. W., *Anal. Chem.*, **26**, 883 (1954).
4. MOORE, F. L., *Anal. Chem.*, **30**, 908 (1958).
5. HYDE, E. K., AND TOLMACH, J., U. S. Atomic Energy Comm. Rept. ANL-4248 (1948).
6. FARIS, J. P., *Applied Spectroscopy*, **12**, 157 (1958).
7. BRODY, J. K., FARIS, J. P., AND BUCHANAN, R. F., *Anal. Chem.*, **30**, 1909 (1958).
8. BUNNEY, L. R., BALLOU, N. E., PASCUAL, J., AND FOTI, S., *Anal. Chem.*, **31**, 324 (1959).
9. HETTEL, H. J., AND FASSEL, V. A., *Anal. Chem.*, **27**, 1311 (1955).
10. NORRIS, J. A., Symposium on Spectrochemical Analysis for Trace Elements, p. 33 (1958) Amer. Soc. Testing Matls., Phila. Pa., 1958.
11. LERNER, M. W., AND PINTO, L. J., *Anal. Chem.*, **31**, 549 (1959).
12. AHRENS, L. H., "Spectrochemical Analysis," Addison-Wesley (1950).
13. JOENSUU, O., "Spectrochem. Anal. of Rare Earth Elements, Using the Stallwood Arc," *Spectrochimica Acta* (in press).
14. FASSEL, V. A., *J. Opt. Soc. Amer.*, **39**, 187 (1949).
15. LERNER, M. W., AND PINTO, L. J., *Anal. Chem.*, **31**, 549 (1959).

CYRUS FELDMAN

SAMPLE STANDS

Over the years various investigators have employed so many different forms of sample for emission spectrochemical analysis and manufacturers and individuals have developed such a multiplicity of designs for holding the samples that the present article can

TABLE 1. ABSOLUTE SPECTROGRAPHIC SENSITIVITIES FOR DETECTION OF RARE EARTHS

Element	Limit of Detection in 10^{-9} g. (millimicrograms)		
	Copper Spark ⁶	Graphite Spark (Zn Buffer) ²	D. C. Arc Y_2O_3 Carrier-Matrix ¹⁰
Y	0.5	5	—
La	2	200	200
Ce	30	200	2000
Pr	30	—	1000
Nd	30	200	1000
Sm	50	200	500
Eu	2	30	200
Gd	20	30	500
Tb	100	—	500
Dy	20	30	500
Ho	20	—	1000
Er	10	—	200
Tm	20	—	200
Yb	1	—	10
Lu	1	—	—

only hope to sketch some of the basic arrangements. Good stands require in common:

(1) Adequate adjustments and sufficiently stable construction to locate and maintain the discharge on the optical axis.

(2) Sufficient insulation to preclude any electrical breakdown.

(3) Construction to withstand thermal radiation from the hottest sources likely to be employed.

(4) An enclosure to prevent extraneous convection currents from affecting the source conditions and to act as a safety control in protecting the operator from accidental shock and from eye burn.

Pin or Electrode Stands

When the sample is in the form of pins or rods, or if the sample is a powder which is to be placed in a cup or crater drilled in a graphite, carbon or other electrode, the pins or electrodes are normally held in clamps, preferably spring-closing, for speed and convenience. If the exposure time is not protracted, so that the electrodes do not burn away rapidly, the electrodes can be set against a swing-out gauge to position the discharge on the optical axis. Normally, however, slow-motion adjustments are provided so that the electrodes may be repositioned as they burn away. Usually, also, a rapid lateral motion is needed if the operator wishes to try to follow the motion of an arc as it wanders around the electrode tip. To define the correct position of the gap, it is customary to use either a separate projection lens and a screen with some form of target marked on it or to include such a projection system within the stand itself.

Petrey Flat or Plane Stand

Frequently a uniform metallurgical sample, free from segregation and of uniform grain size, can be most readily obtained by quick chill-casting a flat disk or by sawing a slice off a bar of metal. A series of such speci-

mens, with one face machined or ground plane and sequentially placed on a specimen table mounted on the optical axis, will reproduce the same optical alignment. A counter-electrode, usually of graphite, is held in a single clamp, and is positioned by a gap spacer. Petrey table attachments are frequently provided with pin stands, to permit interchangeable use of pins and flats.

Solution Stands

Solutions have been handled in a wide variety of ways. Some require special stands or attachments to pin stands. Others (b and f below), may utilize a conventional pin stand. The most common arrangements are:

(a) *Hitchen or Zehden Spark Stands* feed the solution into a spark gap through a small bore hole drilled down the axis of the lower electrode. The rate of feed is determined by the "head" of the solution container above the gap. The arrangement has never been developed to provide such a rapid and convenient procedure as later solution methods.

(b) In the *Porous Cup Method*, devised by Feldman, the solution is contained in a thin-walled upper electrode. The walls are sufficiently permeable to permit the solution gradually to feed through to the bottom. Here it is vaporized by the spark. The porous cup is a simple and convenient method of analysis, but it has been found difficult to obtain coefficients of variation better than 3-5 %, primarily because of varying permeability for different elements from electrode to electrode. If highly acid solutions are used, the electrode clamps and interior of the spark stand must be of acid resistant construction.

(c) The *Rotating Disk Method* of sampling solutions or oils is probably currently more widely used than any other single technique. The sample is contained in a porcelain or other solution resistant boat. The lower electrode consists of a graphite disk which is mounted on a stainless steel or graphite shaft, rotated at the rate of 10-30 r.p.m. The

disk drags solutions up into the spark gap. Most common elements can be detected at concentrations of .1 to 5 parts per million. Coefficients of variation better than 1 % are frequently obtained with direct reading spectrometers. The method is fast and convenient.

(d) In the *Rotating Platform Technique* the solution is contained in a slight depression in a horizontal graphite electrode.

(e) DuBois has used an aspirator to introduce a sample into the discharge through a hole drilled in the lower electrode. Good sensitivity and precise quantitative results are achieved.

(f) Zink¹ has introduced an interesting and useful "*Vacuum Cup*" electrode for the analysis of solutions. A capillary hole (No. 60 or 70 drill) is axially drilled to a depth of approximately one-half inch in the top of a hemispherically shaped electrode. This capillary is opened to the side of the electrode with a small hole (about No. 30 drill). The outside of the electrode is trimmed to a slightly smaller diameter to just below the side hole and a "Teflon" cup with a center hole to fit the trimmed electrode is slipped over the top. Thus, the cup fits about the capillary portion of the electrode and provides a reservoir for the solution to be analyzed.

The "*Vacuum Cup*" operates by means of the reduction in pressure in the lower portion of an arc discharge. The solution is drawn from the cup up through the capillary and into the arc column. For best results, about one milliliter should feed into the discharge in 80 seconds.

(g) *Copper and Graphite Sparks*. Tomkins, Nachtrieb, and Fred² developed a procedure of drying quantitative amounts of solution on the tops of flat copper electrodes, which were then used as the upper and lower electrodes in a spark discharge. Zotov and Morris have used graphite electrodes in a similar procedure. Before evaporating the solution on the electrode top, the electrode should be coated by means of a 2 % "Lucite" solution in

acetone, as large increases in sensitivity and precision result. Both methods yield very high sensitivities and relatively good precision.

Powdered Samples

Powdered samples, like liquids, have been treated in many ways, of which the most useful seem to be:

(a) The powdered sample is contained in a cavity drilled in a lower electrode. A *buffer* of graphite, zinc powder or many other materials may be admixed with the sample to promote uniform burning, or to establish excitation conditions which will suppress inter-element effects, or to encourage uniform vaporization despite differing matrices. Sometimes the sample is fused, typically with lithium or sodium carbonate or tetraborate, and then ground. This produces a more uniform sample and introduces a buffering agent. Some spectrographers prefer to compress or briquet their powders (up to 50,000 pounds/square inch pressure) to still further promote uniformity of burning.

A direct current arc is most commonly used to burn the sample, but all of the circuits described under sources have been employed.

More specialized techniques are:

(b) The *Carrier Distillation* method was developed by Scribner as a device for volatilizing the common impurity elements in uranium into the arc discharge without exciting the nearly continuous uranium spectrum itself. The sample, as oxide, is mixed with high purity compounds of Ga, Ag, F, or In, depending on the specific elements to be analyzed and their relative volatilities. In a DC arc, the trace elements evaporate with the carrier, and only after this has been completely evaporated does the uranium spectrum appear. Unfortunately, the method does not assist in analyzing such impurities as the majority of the rare earths and other heavy elements in uranium. The technique may be applied to the determination of light

elements in refractory materials other than uranium.

A somewhat reverse arrangement is sometimes employed to retard the evaporation of such elements as Hg, Pb, Cd, and Zn. Te or Se mixed with a sample may increase the burning time by five- to tenfold, improving sensitivity and repeatability.

(c) A *Rotating Disk Stand or Attachment* can be used to excite powdered samples after briquetting the finely ground powder into a $\frac{1}{2}$ " diameter disk $\frac{1}{8}$ " thick and sparking to the upper periphery. Such a briquetted sample, held in a clamp, can serve as the lower electrode of a spark discharge. Coefficients of variation under 1% can be obtained with a direct reader.

(d) *The Tape Machine*. Danielsson, Sundkvist and Lundgren³ have a procedure of feeding finely powdered samples onto a traveling belt of "Scotch tape," scraping it level and feeding it into a spark gap between graphite electrodes. The tape moves at a sufficient rate to ensure that the breakdown for each new half cycle of the spark strikes fresh material. The method introduces material to the spark at a steady and repeatable rate, and coefficients of variation of 1% or better are frequent with a direct reading spectrometer.

(e) *The "Stallwood Jet"* is a recently developed accessory for improving the stability of the arc discharge. It is based on Stallwood's⁴ investigation of selective volatilization and element interference effects in powder analyses. The accessory consists of an attachment to fit about the lower electrode and blanket the arc discharge with an atmosphere of controlled composition, usually a mixture of argon and oxygen, or argon by itself.

The effect of the "Stallwood Arc" is to stabilize the discharge both mechanically and chemically. The mechanical stabilization is produced by the prevention of arc wandering through the controlled air blast surrounding the arc, plus the removal of heat

from the lower electrode. In addition, the surrounding gaseous discharge effectively stabilizes the arc chemically by the increase in oxidizing potential and/or the reduction in cyanogen background. Thus, higher sensitivity is achieved through the decrease in background. In addition, selective volatilization and matrix effects are greatly reduced through the stabilized lower sample temperature.

REFERENCES

1. ZINK, T. H., *Applied Spectroscopy*, **13**, 94 (1959).
2. FRED, MARK, NACHTRIEB, NORMAN H., AND TOMKINS, FRANK S., *J. Optical Soc. Am.*, **37**, No. 4, 279-288, April, 1947.
3. DANIELSSON, A., SUNDEKVIST, G., AND LUNDGREN, F., 1959 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.
4. STALLWOOD, B. J., *J. Opt. Soc. Am.*, **44**, 171 (1954).

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SAMPLING

The widespread use of spectroscopic instruments as well as other physical instruments is the outstanding feature in the development of analytical chemistry during the past two decades. Many diverse types of these instruments are being employed in industry as "stream analyzers" to provide automatic control of processes. These developments were stimulated by the need for frequent, accurate, and rapid analyses because of ever-narrowing specifications for raw materials and finished products.

In emission spectrometry, the principal improvements have been in the optical and detecting systems. One spectacular development has been the direct-reading spectrometer, in which the photographic emulsion has been replaced by a number of photomultiplier tubes and associated electronic circuits as a detecting system. This has resulted in a substantial reduction of both time and error in analysis.

To secure the best possible precision and

accuracy with these instruments, the analyst is confronted now with sampling problems that were not apparent before. It is remarkable that routine, rapid, accurate, and precise analyses are possible from some 70 elements by using only 10 milligrams of sample. How can a few milligrams that are truly representative be chosen from, say, 50 tons of material? This appears to be an impossible situation. Yet this choice is made daily with a great deal of success in thousands of laboratories throughout the world. Obviously, this small sample is not chosen in a haphazard manner. In practice, a very large sample is taken in a predetermined way and subsequently prepared to make it homogeneous.

Even then, the spectrographer is faced with problems associated with the vaporization of this sample and the excitation of the spectrum. The volatilization of the sample depends on its physical and chemical properties and the surrounding environment. Heating the sample by the electrical discharge usually results in chemical reactions that affect the rates of volatilization of the elements composing the sample. In a metal or alloy, oxides are formed that are usually refractory. During the period in which these oxides are formed, the observed intensity ratios change and in time approach equilibrium.¹ This period is called the pre-burn or pre-spark time. If the discharge occurs in nitrogen or in an inert gas, such as argon, the intensity ratios are usually constant throughout the time the discharge occurs.² If the sample is mixed with graphite and the mixture placed in a graphite cup, some elements, such as tantalum, form very refractory carbides, and low sensitivity results. However, differences in volatilization rates may be beneficial. For example, the higher vaporization rates of the oxides of most impurities in uranium were utilized in the carrier-distillation method.³

Experience has shown that most of the samples analyzed by emission spectrometry

fall into two general categories. In the first category, the sample is a good electrical conductor and therefore a metal or alloy. It is also homogeneous or can be made so by remelting. Spectrometric standards are available, and the analysis may be performed with a minimum of sample preparation. The second category is composed of samples that are poor electrical conductors. (This group also includes those metals and alloys that cannot be readily analyzed because of the lack of standards, and therefore must be subjected to some chemical preparation, such as dissolution in mineral acids.) This category is characterized by the general lack of readily available standards although the preparation of synthetic standards is usually a straightforward procedure. Because of the poor electrical conductivity of the sample, it is placed in intimate contact with a material of moderate electrical conductivity, such as graphite.

Segregation in metals and alloys nearly always originates in the solidification process. The segregation pattern may be altered by subsequent thermal or mechanical treatment. The only exceptions are those materials that have been formed by welding, cladding, electroplating, and other similar processes. Therefore, some consideration should be given to the factors that influence homogeneity in the solidification of liquid metals and alloys.

The thermal conditions in the mold govern the cast structure, that is, the grain size and shape, the orientation of the grains, and the segregation of solutes and insoluble impurities. The mold has two major functions: (1) it determines the shape of the casting; and (2) it extracts the superheat and latent heat of fusion liberated during solidification. The size and shape of the mold, the thermal conductivity and specific heat of the material from which the mold is made, the mold temperature at the time of pouring, the pouring temperature, and the thermodynamic properties and mass of the cast material

have a profound effect on the structures produced in freezing. The material closest to the mold wall is the first to freeze, creating a thin shell that shrinks away from the mold walls as it cools. A thermal gradient is established between the mold walls and the center of the casting. The material then solidifies as long, columnar crystals with a dendritic structure in the direction of the maximum thermal gradient. The trunk and branches of the dendrite are composed of the first material to freeze, which is nearly always purer than the average composition of the melt. Impurities and alloying constituents are rejected to the liquid phase and eventually solidify between the dendrites and in the center of the casting. The last material to freeze does so as equiaxed grains. Gases also concentrate in these enriched zones, particularly at the center. As the temperature decreases, the solubility of the material for gases also decreases, and these gases are evolved as bubbles that rise through the remaining molten metal. Very often, these bubbles become entrapped as solidification progresses, and a porous casting results. Since the porosity occurs in enriched regions, it is not surprising that poor analytical results are obtained when such samples are used.

Another factor involved in solidification is the shrinkage of the dendrites as they cool. If this is severe enough, interdendritic channels may be formed, extending sometimes to the surface of the casting. The low pressure created may draw enriched liquid metal into the channels. This explains the formation of "tin sweat" in tin-bronze castings. A less severe form of this type of segregation in aluminum-alloy castings has also been observed.

Samples of metals and alloys for spectrometric analysis are cast into a metal mold to promote rapid freezing. Since the last metal to freeze is usually richer in impurities and alloying elements, areas near the top of the mold or near a gate are avoided. If the

casting is square in cross section, the corners are also avoided, since these regions contain the boundaries between two systems of columnar grains (Figure 1b). Until recently, little attention was given to mold design. From the above discussion on solidification, it is obvious that better precision would be obtained if the surface to be analyzed exposed the ends of the columnar crystals rather than their sides. In this way, the discharge would cover a larger number of grains. Today, many laboratories are using a new type of mold^{4,5} that promotes solidification preferentially in one direction only rather than in two or more. A ceramic ring is placed on a large copper block to form the mold (Figure 2). When the sample is cast into this mold, it solidifies mainly from the bottom to the top. By cutting a slice from the bottom, the ends of the columnar crystals are exposed (Figure 1a). Any area on this exposed surface may be used for spectrometric analysis. However,

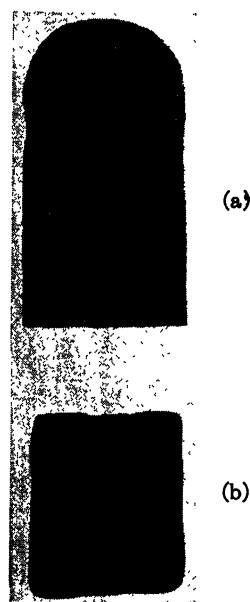


FIG. 1. (a) Structure of sample cast in copper-chill-plate and ceramic-sleeve mold. (b) Structure of sample cast in permanent cast-iron mold.

sometimes a chill-cast sample desirable for emission spectrometry because of its homogeneity may be too hard to machine to provide material for chemical analysis. To overcome this difficulty, another suitable mold has been designed and used by Kennedy and Smith.⁶ The mold consists of two sections hinged together (Figure 3). One section is made of copper and has a cavity machined in it the size and shape of which are such as to produce a chill-cast disc when molten metal is poured into it. The other section is made of carbon steel that has a hole in it so that a shell mold may be inserted. The resultant casting consists of two parts: (1) the lower half is a chill-cast disc used for spectrometric analysis and (2) the upper half is a slowly cooled piece that may be drilled to provide a sample for chemical analysis. This mold is particularly useful in the analysis of cast iron.

Many alloys cannot be cast to produce a homogeneous sample. These materials are usually analyzed by using a solution technique. This method of approach is often tedious and time-consuming, and therefore not suitable for routine laboratory analysis. A simpler procedure is to move the sample during excitation so that a relatively large area is covered by the discharge. This technique has been applied to the analysis of zinc spelter and resulted in a fivefold decrease in standard deviation for the analysis of this material for aluminum and tin.⁷

Samples with poor electrical conductivity are ground and mixed with graphite powder, and packed into a hole in the end of a graphite rod. Samples of this type may be rocks and minerals that by their nature are heterogeneous. Usually a buffer material is added for several reasons. The buffer in this case is added to create a common matrix and stabilize the temperature of the sample electrode. In many instances, this buffer may actually be a flux, and the sample is fused with the buffer material to eliminate heterogeneity prior to mixing with graphite pow-

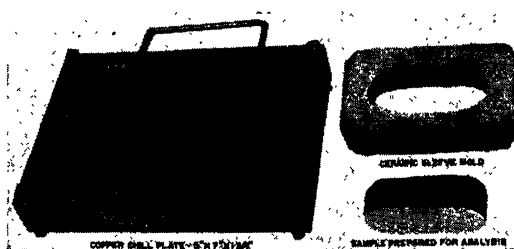
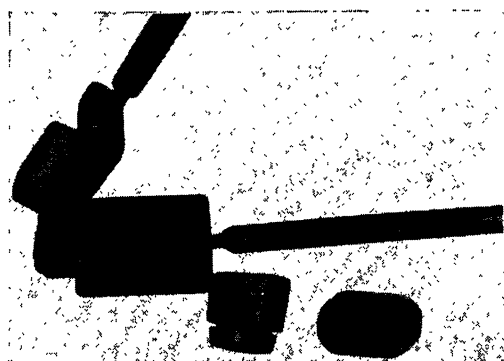


FIG. 2. Copper chill plate, ceramic sleeve, and the resultant cast sample.



(Courtesy of Applied Spectroscopy and American Cast Iron Pipe Company)

FIG. 3. Combination chemical and disc mold.

der. Since the sample contains elements having different rates of volatilization, the sample is usually burned to completion. The buffer may also contain an element, such as molybdenum,⁸ which is used as an internal standard with a fixed concentration. Samples may be vaporized from a solution by the porous-cup⁹ and rotrode techniques.¹⁰ These procedures have several advantages over powders: (1) the solution remains relatively cool during vaporization and hence little or no preferential volatilization occurs; (2) any effects due to metallurgical history or heterogeneity are nullified by the dissolution of the sample; (3) synthetic standards may be prepared relatively easily. However, erosion of the electrode holders in the excitation stand by the solution can be a problem.

REFERENCES

1. KAISER, H., *Spectrochimica Acta*, **1**, 1 (1939).
2. GERLACH, W., *Metallwirtschaft*, **43**, 1088 (1937).

3. SCRIBNER, B. F., AND MULLIN, H. R., *J. Res. Nat. Bur. Standards*, **37**, 379 (1946).
4. DAMIAN, S. W., private communication.
5. GUYER, H., *Met. Ital.*, **49**, 411 (1957).
6. KENNEDY, W. R., AND SMITH, R. N., *Applied Spectroscopy*, **14**, 53 (1960).
7. DOTSON, C. L., *Applied Spectroscopy*, **9**, 33 (1955).
8. FRED, M., NACHTRIEB, N. H., AND TOMKINS, F. S., *J. Opt. Soc. Am.*, **37**, 279 (1947).
9. FELDMAN, C., *Anal. Chem.*, **21**, 1041 (1949).
10. PAGLIASSOTTI, J. P., AND PORSCHKE, F. W., *Anal. Chem.*, **23**, 198 (1951).

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SEMIQUANTITATIVE INDUSTRIAL CHEMICAL ANALYSIS

The use of emission spectroscopy to determine the composition of a wide variety of samples has been developed to the point where it is now an indispensable technique in analytical work. For many years the spectrograph was an important, but limited, tool because the chemists had not developed preparative techniques of wide versatility. Much work was done by physicists to identify spectrum lines associated with the elements and by chemists to develop unique quantitative procedures for specific elements in a given alloy or a particular repetitive sample system. These procedures are widely used today in control work to monitor production systems. For the majority of random samples, however, the spectrograph was used only to specify the qualitative composition of the sample. This condition no longer exists and today the emission spectrograph is often the first tool used to establish the approximate amounts of the elements present in an unknown material. Generally this results in sufficient data to solve a particular problem or to permit a more intelligent selection of subsequent test procedures. This article will describe a general technique which considerably broadens the scope of application of the emission spectrograph.

Spectrographic laboratories are frequently confronted with the necessity of analyzing a

wide variety of materials with speed and accuracy. The samples are non-repetitive and are generally of an unusual nature. The time required and the cost of establishing a specific quantitative spectrochemical procedure for each type of sample are prohibitive. Further, qualitative or noncommittal answers, such as major, minor, and trace, seldom have enough meaning to answer a problem satisfactorily.

Spectroscopists have devoted considerable time and effort to the development of methods which are capable of analyzing any sample for its constituents with an accuracy in the intermediate range between the qualitative and precise quantitative approaches. The term "semiquantitative" is used to describe these methods which yield results with accuracies falling within a factor of $\frac{1}{3}$ to 3 times the amount present.

In general, a practical semiquantitative method should be rapid, inexpensive, applicable to milligram-size samples, and easily applied by previously untrained personnel after 4 to 5 weeks training.

Several methods of this type have been reported in the literature and it has been the subject of considerable investigation by Subcommittee II on Fundamental Methods, ASTM Committee E-2 on Emission Spectroscopy. An excellent summary and classification of the various methods in the literature, along with the criteria for a universal method, can be found in the ASTM Committee publication.⁵

The major obstacle to overcome in the development of a method of universal applicability is the marked effect that the presence of different materials in the sample has on the behavior or line intensity of each element being determined. This influence of the major constituents is easily demonstrated. For example, identical exposures of samples of sodium chloride and lead oxide containing equal amounts of copper will not yield copper spectrum lines of equal intensity. One may choose to ignore these matrix effects and ac-

cept the accuracy obtained. However, this will result in errors which exceed the limits imposed on semiquantitative analysis.

There are several approaches that can be used to correct for or minimize these matrix effects depending on the accuracy desired. One approach is to compare the unknown spectrum with spectra of known samples. After the initial comparison, another known mixture is prepared and its spectrum compared with the unknown. This process is repeated until a satisfactory match is obtained. The time required for the analysis of each sample is considerable, and although this procedure is useful in specific applications, it cannot be considered as a method of general applicability.

A second method is to compensate for the matrix effects by correcting for the differences which occur in the various matrices. An experienced analyst can often judge the effect of the matrix elements and estimate the appropriate correction. This requires considerable experience in analyzing a wide variety of materials and cannot be performed by an operator with limited experience.

A more elaborate method of correction is that developed by Harvey.⁶ He has published a book containing correction factors for spectrum lines in a large variety of matrices. The concentration of an element is determined by multiplying its spectrum line intensity by the predetermined concentration factor for that particular matrix. When the matrix is a mixture of elements, a new factor must be established. Addink¹ does this by adding two different amounts of the element he is determining to separate portions of the sample. Concentration factors are applied and the difference between the two analyses should be the difference in the small amounts added. If the difference is not correct, the factor is adjusted and the new concentration factor used for the actual sample analysis. Methods utilizing concentration factors have been quite successfully applied

by many spectrographic laboratories. They do, however, require considerable effort initially to establish all of the necessary factors which vary depending on the characteristics of the individual spectrograph. Also, the presence of more than one matrix element makes it difficult to determine the appropriate factor.

The most widely accepted method in use today and the one which is by far the most universally applicable is the technique of dilution. The basic aim of this approach is to incorporate all samples, regardless of their compositions, into a common matrix material. This dilution, with a buffer or carrier material, causes the elements present in all samples to behave in a manner approaching their behavior in the pure matrix material. To a satisfactory degree, one then assumes that through the dilution procedure all samples, regardless of their origin, are similar and burn similarly in the arc. In other words, the sample is analyzed as an impurity in the common matrix. Only one set of standards, made up in the common matrix material, is necessary for all types of samples.

Much has been written concerning the choice and function of diluent materials. Listed in the Table 1 are several of the diluents used by the investigator(s) indicated. Reference to methods described in the literature also reveals a large variation in the sample dilutions, the exposure conditions, the optical alignments, and the electrode combinations being utilized.

A description of the method the authors use will serve to illustrate a typical semiquantitative procedure. It was designed to permit either a rapid visual estimation of concentration, or the more accurate densitometric evaluation.

The matrix used is a mixture of 40 parts graphite, 50 parts lithium carbonate, and 1.0 part germanium dioxide. Graphite was incorporated into the matrix because of its ability to carry the sample into the arc, thus eliminating excessively long burn times. In

TABLE 1

Diluent	Investigator(s)
Barium nitrate + ammonium sulfate	Fitz, Murray ⁴
Copper oxide + graphite + germanium dioxide	Jaycox ⁷
Gallium oxide	Scribner ¹¹
Graphite	Mitteldorf, ⁸ Waring, Annell, ¹⁵
Graphite + germanium	Strock ¹⁴
Graphite + lithium carbonate	Smith, Mattarella ¹²
Graphite + molybdenum + bismuth	Bachelder ³
Graphite + nickel oxide	Oshry, Ballard, Schrenk ¹⁰
Graphite + zinc oxide	Standen ¹³
Lithium carbonate	Weaver, Brattain ¹⁶
Lithium carbonate + gallium oxide	Mohan, Fry ⁹
Lithium carbonate + vanadium pentoxide	Alexander, Nusbaum ²

addition, it reduces fractional distillation of the elements from the sample during the exposure. Lithium carbonate was selected because of its usefulness in reducing matrix effects. It also enhances the spectrum lines of many elements and thus increases detectability. Germanium was chosen as the internal standard because of its average burn characteristics relative to the majority of the elements to be determined.

The sample-to-matrix ratio is maintained at 1 part sample and 9 parts matrix. This dilution has been found to suppress adequately inter-element effects of a wide variety of sample matrices. A commercially available 0.180 inch diameter graphite electrode is used. The undercut cup has the dimensions of 0.0938 inch in depth and 0.125 inch in diameter. The counter electrode is a pointed, 0.125 inch diameter, graphite rod. The total charge is 20 milligrams (2 milligrams of sample) and is entirely consumed during the exposure.

The sample is burned in a d-c arc at 5 amps for 15 seconds. The current is then increased to 15 amps for 60 seconds. The initial

low amperage prevents the charge from jumping out of the electrode crater and the higher amperage insures volatilization of refractory materials and a complete burn-out of the sample. The spectra are photographed on Kodak Spectrum Analysis Number 1 plates through a four-step sector wheel which transmits approximately 100, 25, 5 and 1 per cent of the incident light.

Standards are prepared for the elements by successive dilution of dry powders, maintaining the same proportions of matrix combination and internal standard. Standards are prepared for each element in dilution steps of 1 mg (50%), 0.3 mg (15%), 0.1 mg (5%), etc., down to the lower limit of detectability. The photographic plates on which the standard spectra are recorded are retained for reference and are used when it is desired to estimate visually the composition of unknowns. A calibration curve for the SA-1 emulsion is constructed which is representative of the region from 2800 to 3300 Angstroms where most of the spectrum lines employed in the procedure are located. Analytical working curves have been prepared covering the ranges indicated in Table 2 using intensity ratios obtained from the relative intensities of various steps of the analytical lines and the germanium internal standard line. The analytical working curves have been placed on a Dunn-Lowry calculating board to expedite calculations.

In many instances a visual estimation suffices. The sample spectrum is superimposed over each standard spectrum in succession and the lines compared. A satisfactory estimate of the composition of the sample can be made within a relatively short time. When greater accuracy is desired, densities of the appropriate lines are measured and the concentrations determined from the analytical working curves.

Sample preparation prior to mixing with the matrix material constitutes one of the most important steps in the entire procedure. This varies considerably depending on the

type and form of the sample as received. Many samples require the application of special techniques.¹⁷ Organic materials must be carefully charred with a flame or ashed. The time and temperature will depend on the material, but both should be kept to a minimum. If the ash weight anticipated is very low, a few milligrams of graphite are added to aid in removing the ash from the container. Liquids are evaporated to dryness and the residue ashed or mixed directly with the matrix. A few milligrams of graphite added during the last stages of evaporation will aid in recovering small residues. Inorganic materials are ground to a fine powder and mixed directly with the matrix material. Metals are converted to salts, or in some instances, filings are added directly to the matrix.

Kodak Spectrum Analysis Number 1 emulsion was chosen to record the spectra because of its relatively high contrast. With this emulsion a greater line density change per change in element concentration is obtained, which is a decided advantage for visual estimation. It is advisable, however, to use a step sector wheel or step filter with the SA-1 emulsion to maintain the spectral lines within a usable optical density range for densitometric measurements. To obtain a workable overlap of densities, the ratios of the steps of the filter or sector wheel should not exceed 5 to 1.

The accuracy of this method has been studied by the analysis of known mixtures prepared in this laboratory, National Bureau of Standards samples, and six standard mixtures used in the ASTM cooperative analysis.⁵ The data indicate that densitometric evaluation of the spectra can be relied upon to produce answers accurate to within ± 50 per cent. The precision obtained is ± 20 per cent. Visual concentration estimations generally will fall within a factor of 3 of the correct analysis, still within the limits imposed on semiquantitative analysis.

The authors have observed an improve-

TABLE 2

Element	Wave-length, Å	Concentration Range	Visual Detection Limit
Germanium	3039.06	Internal Standard	
Aluminum	3064.30	50%-2%	0.0005%
	3082.16	2%-0.005%	
Antimony	2877.92	50%-0.1%	0.01%
Arsenic	2349.84	50%-0.5%	0.5%
Barium	3071.59	50%-0.1%	0.05%
Bismuth	3087.72	50%-0.01%	0.001%
Boron	2496.78	50%-0.05%	0.01%
Cadmium	3261.06	50%-0.1%	0.05%
Calcium	3179.33	50%-0.1%	0.05%
Chromium	2835.63	50%-0.05%	0.001%
	3021.56	0.3%-0.002%	
Cobalt	3044.00	50%-0.01%	0.005%
Copper	2961.16	50%-0.5%	0.0001%
	3247.54	5%-0.001%	
Indium	3256.09	50%-0.005%	0.0005%
Iron	3021.07	50%-0.003%	0.001%
Lanthanum	3245.12	50%-0.1%	0.05%
Lead	2802.00	50%-0.04%	0.005%
	2833.07	0.5%-0.01%	
Magnesium	2802.70	50%-0.001%	0.0005%
Manganese	2949.20	50%-2%	0.0001%
	2801.06	5%-0.0005%	
Molybdenum	3158.16	5%-0.005%	0.001%
Nickel	3050.82	50%-0.002%	0.001%
Phosphorus	2553.28	50%-1%	0.5%
Potassium	3446.72	50%-1%	1%
Silicon	2881.58	50%-0.005%	0.005%
Sodium	3302.32	5%-0.01%	0.005%
Strontium	3464.46	20%-0.1%	0.05%
Tin	3175.02	50%-0.01%	0.005%
Titanium	3078.64	50%-0.003%	0.001%
Tungsten	2944.40	50%-0.1%	0.05%
Vanadium	3185.40	3%-0.005%	0.001%
Zinc	3345.02	50%-0.2%	0.1%
Zirconium	3438.23	50%-0.01%	0.005%

ment in accuracy with the addition of bismuth (along with the germanium) for use as an internal standard for the more volatile elements such as cadmium, lead, and zinc. The addition of an internal standard such as zirconium would increase the accuracy obtained for the refractory elements. Also, the analytical results for certain of the elements would be improved through the use of additional germanium internal standard lines. However, each of these additional steps tends

to make the procedure more complicated with resultant increase in analysis time, greater chance for arithmetic error, and longer personnel training time.

It is important when utilizing a method of this type that adequate controls be established to prevent relatively large errors from entering the procedure over an extended period of time. Variations in excitation conditions, instrument alignment, sample preparation, emulsion calibration or speed, and photographic processing must be minimized and corrected for. It is recommended that standard mixtures be analyzed periodically and corrections made accordingly.

In the authors' laboratory, the procedure described is applied to over 100 different samples each week. Water, inorganic and organic chemicals, oils, dust collected in filtering and air conditioning systems, sludges and residues from tanks and pipes, metal chips, solders, plastics, floor sweepings, photoconductors, plating solutions, minerals, corrosion products, biological materials, alloys, ores, and bearings are examples of the general types of materials that have been analyzed by this technique. The examples illustrate the versatility of the procedure and also the variety of problems to which it can be applied. The time required for these analyses varies from 15 minutes to 2 hours per sample depending on the form of the sample as received, the complexity of the spectrum obtained, the number of elements sought, and the degree of accuracy required.

Considerable effort is required initially to prepare standards, select spectrum lines, and establish the analytical curves. However, this effort is easily justified when the variety of samples that can be analyzed by a single procedure, the speed of the analysis, and the cost of obtaining the same information by other means are considered. In addition, many of the samples which can be analyzed by this technique are of such a size and nature that they defy conventional chemical analysis.

The development of these semiquantitative techniques of universal applicability represents one of the major advances made in terms of the practical application of the spectrograph as an analytical tool in industry.

REFERENCES

1. ADDINK, N. W. H., *Rec. Trav. Chim. Pays-bas*, **67**, 690-6 (1948).
2. ALEXANDER, G. V., AND NUSBAUM, R. E., *Anal. Chem.*, **24**, 793-5 (1952).
3. BACHELDER, M. C., *Anal. Chem.*, **21**, 1866-9 (1949).
4. FITZ, E. J., AND MURRAY, W. M., *Ind. Eng. Chem. (Anal. Ed.)*, **17**, 145-7 (1945).
5. FREY, D. L., *ASTM Bulletin*, No. 216, 29-32 (1956).
6. HARVEY, C. E., "Method of Semiquantitative Spectrographic Analysis," Applied Research Laboratories, Glendale, Calif. (1947).
7. JAYCOX, E. K., *Anal. Chem.*, **27**, 347-50 (1955).
8. MITTELDORF, A. J., "The Spex Speaker," Vol. II, No. 2 (1957).
9. MOHAN, P. V., AND FREY, D. L., *Applied Spectroscopy*, **12**, 90-5 (1958).
10. OSHEY, H. I., BALLARD, J. W., AND SCHRENK, H. H., *J. Opt. Soc. Amer.*, **32**, 672080 (1942).
11. SCRIBNER, B. F., *J. Research NBS*, **37**, 379-89 (1946).
12. SMITH, R. W., AND MATTARELLA, S. P., "Methods for Emission Spectrochemical Analysis," 423-7, ASTM, Philadelphia, Pa. (1957).
13. STANDEN, G. W., *Ind. Eng. Chem. (Anal. Ed.)*, **16**, 675-80 (1944).
14. STROCK, L. W., *Applied Spectroscopy*, **7**, 64-71 (1953).
15. WARING, C. L., AND ANNELL, C. S., *Anal. Chem.*, **25**, 1174-9 (1953).
16. WEAVER, J. R., AND BRATTAIN, R. R., *Anal. Chem.*, **21**, 1038-41 (1949).
17. YOE, J. H., AND KOCH, H. J., "Trace Analysis," Chap. 24, John Wiley & Sons, Inc., New York (1957).

J. A. LEYS AND R. L. DEHM

SEMIQUANTITATIVE SPECTROCHEMICAL ANALYSIS

As a secondary method, spectrochemical analysis depends on the use of standards which, when bracketing the unknown, permit the analyst to make determinations by

interpolation. The principal requirement for a set of standards, that the materials match as closely as possible the unknowns, can only be met when the spectrochemist has a pretty good idea what his unknown is beforehand. Thus, the analysis of an ore, sludge, dust, slag, corrosion deposit, ash, residue or, simply, "gook", presents a problem not solvable by the use of specific standards. In their place are used universal standards, ones which are applicable to almost any sample by diluting it so the matrix resembles that of the standards. For example, with the Spex G Standards, which contain 43 elements at identical low concentrations in a graphite base, samples are first diluted with graphite. The matrix effect is thus bypassed.

Before going into further detail on analytical methods, it would be well to trace the history and development of semiquantitative analysis. Fry¹ classified the attempts to develop a universal method of semiquantitative analysis under five headings:

- (1) Disregard the matrix effects.
- (2) Compare the unknown spectra with spectra of synthetic samples.
- (3) Correct for matrix effects.
- (4) Select internal standard for each element group.
- (5) Dilute unknowns with a large amount of some material: (a) an alkali-metal salt; (b) other miscellaneous metal or metal salt.

As would be expected, the first of these is subject to the most error. Ignoring the matrix effect results in little better than a *qualitative* analysis. Equally significant, an element reported absent may be present in sizable concentrations if the behavior of the matrix is ignored. Methods in category (1) are thus primarily of historical interest.

In 1938, Slavin² developed the so-called total energy concept. He postulated that if a sample is burned to completion the intensity of a particular line will be proportional to the number of atoms emitting it—in other words, the concentration. Burning nine different NBS samples to completion, he was

able to obtain a straight-line plot of the density of the calcium 3179A line *vs.* the weight of calcium in the respective sample. On this basis, he tentatively concluded that *any* element in *any* matrix could be measured merely by determining the proportionality constant relating the line density to the mass of the element *under the conditions used in a particular laboratory*. Although Slavin did not succeed in developing a universal semiquantitative method on this basis, he made an extraordinary contribution by showing how essential a complete burn is.

The total energy concept having pointed the way to better semiquantitative methods, others were developed, some along the lines of the second category given above. For instance, suppose one has to analyze samples of Mesabi ore for trace elements. One carefully prepares a series of synthetic Mesabi ores varying the trace-element concentrations. Using these as standards, accuracy can be almost quantitative. The main drawback of this second approach is that such standards are almost useless for the analysis of, say, a KNP fertilizer for trace-element content.

To summarize our appraisal of methods (1) and (2), the former should be used for *qualitative* analysis only. The second, while extremely useful in specific applications, obviously begs the question. It presupposes that the general composition of the sample is known. Very rarely is this true.

When the importance of the matrix became apparent, workers sought means for circumventing its influence. Correcting for matrix behavior, the third approach, was that developed by Harvey³ in 1947. He made exhaustive studies of the effects on spectral intensity of a wide variety of common substances. These were then converted into correction factors and published in tables. The criticism of this system, like that of the previous one, is that it is not applicable to a *complete* unknown. One must have a good idea of the material being analyzed be-

EMISSION SPECTROSCOPY—LIGHT

fore knowing which correction factor to use. Moreover, Harvey's factors vary considerably depending on the characteristics of the individual spectrograph.

The fourth approach is probably the most unwieldy as a general method. If one wants to determine calcium in an unknown, he first adds a known amount of an element resembling calcium, for example, magnesium. From the way in which the magnesium lines behave, he can correct for and therefore estimate the concentration of calcium. Again, although there are occasions where the method is useful, it has two shortcomings. It requires the use of a large number of internal standards for each sample; it precludes the determination of those elements which are themselves added as internal standards. But, like the Harvey method, it is frequently a handy method, especially when no standards are available and a proximate determination of a particular element is needed.

The last in our outline of techniques is the category into which the Spex method falls, i.e., dilution. Dating back to 1907, at least twenty papers in the literature make use of this technique. It is by far the most universally applicable, the simplest and least subject to error.

The basis of the Spex adaptation is a powder called Spex Mix. This consists of compounds (mostly oxides) of 43 common elements weighed out so that each element is present in exactly the same concentration. That is, enough silver oxide is weighed out to yield 1.00g of silver; enough antimony oxide to yield 1.00g of antimony; enough calcium carbonate to yield 1.00g of calcium, etc. Separately, each compound is first ground down to -200 mesh and, after being weighed, the compounds are ball-milled for many hours to assure uniformity.⁴ Calculation will give the figure of 1.34 % concentration for every element present.

The actual elements present in Spex Mix are listed below:

Ag	Be	Co	Fe	Mg	Ni	Si	Th	W
Al	Bi	Cr	Ge	Mn	P	Sn	Ti	Zn
As	Ca	Cs	Hg	Mo	Pb	Sr	Tl	Zr
B	Cd	Cu	K	Na	Rb	Ta	U	
Ba	Ce	F	Li	Nb	Sb	Te	V	

The G standards are made by diluting Spex Mix with high-purity graphite. The actual graphite chosen is United Carbon Products Co., UCP-2, -100 mesh. The coarse particles in this material have relatively little tendency to fly out of the electrode cup during burning, a factor often overlooked when poor precision is a problem. Standard G-1 contains 0.100 % of each of the 43 elements. It is made by mixing 0.100 weight units of Spex Mix with 1.24 weight units of graphite. Containing 0.010 % of these elements, G-2 is made by diluting G-1 by a factor of 10 with graphite. The procedure is repeated for G-3 and G-4, the last containing 1 ppm of the elements.

For determination of the rare earth elements, there are analogous standards. Rare Earth Spex Mix contains 5.28 % of the following 16 elements:

Ce	Er	Gd	La	Nd	Sm	Tb	Yb
Dy	Eu	Ho	Lu	Pr	Sc	Tm	Y

The Rare Earth L Standards consist of a set of four at 0.5 %, 0.05 %, 0.005 % and 0.0005 % levels for each of the 16 elements in a lithium carbonate base.

For the determination of noble metals, a preparation called Noble Metal Spex Mix containing 9.32 % of the following elements is used:

Au	In	Pt	Ru
Ga	Ir	Re	
Hf	Pd	Rh	

The Noble Metal G Standards contain the above elements in a graphite base at 0.5 %, 0.05 %, 0.005 % and 0.0005 % levels.

An unknown powder is brought into the laboratory. Let us proceed to analyze it hypothetically. We take 10 mg of the sample and mix it with 90 mg of graphite to obtain a 1:10 dilution. To determine elements

above 1 %, a second ten-fold dilution is required and a third for elements above 10 %. The Mixer/Mill is recommended for the dilution operations. With it, a plastic ball shakes the materials to be mixed in a plastic vial electrically for 10–60 seconds. The shortest mixing time possible is desirable in order to keep the grinding action to a minimum.

We prepare the following samples:

x the original unknown diluted with graphite 1:9

$.0x$ the original unknown diluted with graphite 1:99

$.00x$ the original unknown diluted with graphite 1:999

The actual technique recommended depends on the accuracy requirements. In a typical procedure, all of these materials are burned to completion on the same plate and under the same conditions as the entire set of G standards. A d.c. arc of 5–10 amperes is employed; the sample electrode is made electrically positive. Typical electrodes used for this work are a shallow-crater, undercut $\frac{3}{16}$ " dia. preform (National Carbon Co. L-3906, UCP 105-S) with a pointed $\frac{1}{8}$ " dia. upper. Whatever the electrode used, the sample must be burned to completion.

Table 1 is a hypothetical example of the kind of results to be expected. Here it was not necessary to dilute the sample to $.00x$ since it was known beforehand that all elements were present below 10 % concentration.

Interpretation of Table 1 would be as follows: the silicon at the 100 times dilution ($.0x$) matches the silicon in G-1. In other words, it contains approximately .1 % at this dilution. Multiplying by the dilution factor of 100, the sample is thus calculated to contain about 10 % silicon.

The copper in this sample at the x dilution matches G-4 and therefore represents about $.000x$ %. Multiplying by the dilution factor, the original sample contains about $.00x$ %.

The silver presents an interesting example

TABLE 1. HYPOTHETICAL EXAMPLE OF ANALYSIS USING G STANDARDS

Material	Intensity of Spectral Lines*			
	Si 2881 A	Cu 3247 A	Ag 3281 A	B 2496 A
x	7	2	0	0
$.x$	6	1	1	0
$.0x$	4	0	0	0
G-1	4	4	4	4
G-2	3	3	3	3
G-3	2	2	2	2
G-4	1	1	1	1

* Visual estimates of intensity: 0 is not detected; 7 is very strong.

in that it is not detected in the original sample but detected by the first dilution. This frequently occurs, the graphite diluent actually tending to improve sensitivity. In this example, the silver concentration is around $.001$ % in the original sample.

Boron is not detected in the sample nor in any of its graphite dilutions. Without standards, it would simply be reported "not detected." One big advantage of the Spex method is that the determination is amplified to read "not detected, less than $.001$ %." We reason thus: since boron shows in all four of the standards, its limit of detection is at least $.0001$ %. This means that $.0001$ % would be detected in $.x$, the first dilution of the sample. Multiplying by 10, as previously, we state that the boron content of the original sample, if present, is less than $.001$ %.

While our own work has been with three types of matrices used as diluents (graphite, lithium carbonate and zinc oxide) for semiquantitative work, others have been chosen and are being used successfully. Jaycox⁶ originally employed cupric oxide diluted in the ratio of at least 9 to 1 with the sample but recently has modified the procedure through the addition of spectrographically pure germanium oxide, added in various proportions with the cupric oxide. Silica has a number of advantages but one drawback: when burned in air, its spectrum has a num-

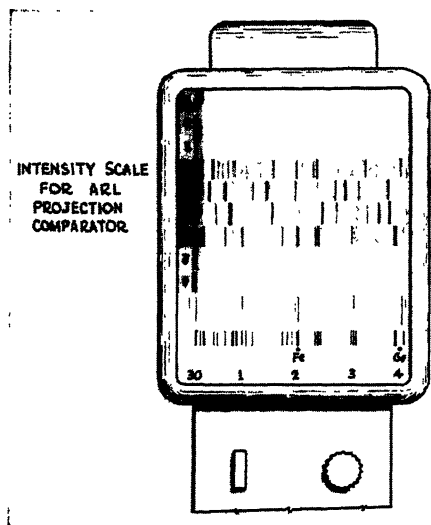


FIG. 1. Hodge scale mounted on the screen of a comparator for matching line intensities.

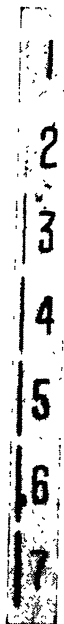


FIG. 2. Graduated density steps as used by Hodge for semiquantitative analysis.

ber of SiO bands which interfere with many lines. Mixtures of graphite and lithium carbonate, first suggested for the analysis of petroleum ashes,⁷ combine the beneficial re-

ducing effects of the former with lithium carbonate's property of stabilizing the d.c. arc.

E. S. Hodge, of Mellon Institute, has devised a scheme for reducing the number of exposures required. His laboratory serves a wide variety of ever-changing research projects and almost every unknown is unique. Rather than running a complete set of standards on each film, Hodge⁵ uses a precali-brated density scale mounted inside the screen of the microphotometer as pictured in Figure 1. Employing a matching technique, he assigns a figure from 0 to 7 depending on which step is best matched by the spectrum line in the sample. For example, suppose at the 1:100 dilution, the silicon 2881A line in a particular sample matches step 3. He refers to a conversion chart previously prepared and finds that 3 represents approximately the same concentration as the silicon content in G-2 or 0.01 %. Multiplying by the dilution factor of 100, he reports approximately 1 % silicon in the original sample.

Part of the conversion chart is shown in Table 2. The most common spectral lines are chosen for each element but room is left for compilation of other lines. At the microphotometer, density numbers are assigned by visually matching the unknown line with a step on scale. Next, by referring to the conversion chart and multiplying by the dilution factor, the approximate % concentration is inserted.

Analysis of "Pure" Materials

Thus far, we have considered the analysis of impure materials consisting of a number of elements rather than essentially one. Another problem is the analysis of a pure material. Here the task again is not only to determine the concentration of impurities present but also assign "less than" figures for those elements not found.

This solution makes use of Spex Mix itself. It is diluted with the sample in several ratios. A comparison of the spectra of the original

material with the diluted materials is the basis of the method. An example will clarify this.

Let us call the sample to be analyzed "A". We first dilute 1.24g of the sample with 0.10g of Spex Mix. This, which we shall call "B", now contains 0.10 % of all of the 43 elements added to the sample. (In other words, if there was 0.5 % iron in sample A to begin with, B will contain 0.6 %. If, on the other hand, the sample contained no germanium, then B will contain 0.1 %.) Next we dilute B with the original sample in the ratio 1B:9A. This we call C which adds 0.010 % of the 43 elements to the original sample A. Likewise D and finally E are prepared by subsequent dilutions.

Table 3 gives the results to be expected in a typical sample.

In Table 3, silicon would be reported .0x %. We notice that the intensity grades from A to B to C but that C, D and E have about the same intensity. The addition of 0.01 % at C resulted in an intensity change but the addition of 0.001 % at D did not. In other words, there must have been at least 0.01 % silicon in the original sample.

TABLE 2. CONVERSION CHART (% CONCENTRATION FROM DENSITY NUMBER) FOR USE WITH HODGE SEMIQUANTITATIVE SCALE

Element	W.L., A	Density Number vs. % Concentration						
		1	2	3	4	5	6	7
Ag	3281							
Al	3093							
As	2350							
B	2498							
B	5535							
Be	2349							
Bi	3068							
Ca	4227							
Cd	2288							
Ce	4187							
Co	3453							
Cr	4254							
Cs	4555							
Cu	3247							

TABLE 3. ANALYSIS OF HYPOTHETICAL SAMPLE OF "PURE MATERIAL" USING SPEX MIX

Desig.	Comp.	Intensity of Spectral Lines*			
		Si 2881 A	Cu 3247 A	B 2498 A	Zn 3345 A
A	Original sample	6	0	7	0
B	0.10% added	4	7	6	4
C	0.010% added	2	4	6	2
D	0.001% added	2	2	6	1
E	0.0001% added	2	1	6	0

* Visual estimates of intensity: 0 is not detected; 7 is very strong.

Copper in the original sample was not detected. But what is the limit of detection in this matrix? We note that copper is detected in the lowest dilution, at 1 ppm and we therefore report: copper not detected, less than 0.0001 %.

The boron content is interesting in that it shows that the "pure" material is really not pure, containing at least 0.1 % of boron. Visually, the 0.1 % addition and the 0.01 % addition of boron appear identical on the microphotometer. Therefore, the original sample must have had at least 0.1 %.

Like copper, zinc is not detected in the original sample. Unlike copper, however, it is not detected at the final dilution. It is reported: zinc, not detected, less than 0.001 %.

Organic Materials

Thus far we have described the analysis of miscellaneous and pure materials. Organic compounds fall in a third category mainly because of the necessity of ashing them before analysis. Either wet ashing or dry ashing may be employed; there are advantages and disadvantages to both. In general, there is a tendency to add impurities in the former and lose impurities in the latter.

A typical dry ashing procedure for the analysis of organic materials would be to start with a one gram sample of the material and then char it in a platinum crucible. The

time and temperature would depend on the particular material but both should be kept to a minimum. After charring, 0.10g of spectrographic grade zinc oxide or lithium carbonate is added and mixed in the crucible for about a minute with a small spatula. The mixture is then ashed at about 450°C and shaken in the Mixer/Mill or otherwise ground to a homogeneous powder. Since this material is to be analyzed against the Spex Z (zinc oxide) or L (lithium carbonate) standards, a small amount of each of the standards can be ashed as "blanks". In other words, an element such as arsenic will volatilize in much the same manner in the standards as in the unknown so that a correction factor will be automatically applied in this manner. A word of caution should be given here. Do not add zinc oxide directly to the organic material before it is charred. Partial reduction of the zinc oxide to the base metal will occur with consequent loss of accuracy.

The procedure given above concentrates the elements in the organic material by a factor of 10. Of course, if one starts with 10g or 100g of the original material, a concentration of 100 or even 1000 is possible. In the final calculations, values are simply multiplied by the appropriate factor.

Although zinc oxide burns smoothly and reproducibly in a d.c. arc without the formation of a refractory bead, many spectrographers prefer to mix it with an equal quantity of graphite before burning. Such a procedure is that developed by G. W. Standen of the New Jersey Zinc Company. His electrode is a $\frac{1}{8}$ " diameter rod with a hole drilled to a depth of about $\frac{1}{4}$ " and burnings are again made to completion.

Accuracy

When the original work on the Spex standards was done, a precision figure of $\pm 30\%$ was claimed. Since that time, many spectrographers have told us that they have attained $\pm 10\%$ by taking densitometric read-

ings and observing precautions ordinarily reserved for quantitative work, such as correcting for background, running samples and standards in replicate on the same plate, etc.

While it is good to know that by spending more time on the problem excellent accuracy may be attained, a balance between the *cost* and the *value* of the analysis should always be maintained. With this in mind, the following will show what returns can be expected from the least effort, the most effort and several intermediate degrees of effort.

Undoubtedly, the simplest method of semiquantitative analysis when any volume is involved is that devised by Hodge. A few hours spent in precalibration of the standards against a stepped intensity scale is rewarded by a large saving in time when samples are run. Hodge reports that for 200 determinations on NBS samples, 90% of all concentrations found fell within the range $\frac{1}{3}$ to 3 times the standardized values. This maximum range is the criterion of semiquantitative accuracy assigned by ASTM.¹

A variation of Hodge's method is to prepare a master plate (instead of an intensity scale) containing an entire set of semiquantitative standards and run under conditions identical with those to be employed for unknowns. Lines on this plate are marked off to facilitate identification. While requiring a good deal more preparatory work, this method has an advantage in accuracy over Hodge's systems. The zinc line at 3345A, for example, will be just as diffuse on both the comparison and the unknown plates and the respective backgrounds will be equivalent, too. Matching is more exact than with the Hodge scale since one does not have to make mental corrections for differences in background and/or line shape. Precision possible with this matching technique is perhaps such that the results will fall between $\frac{1}{2}$ and twice the correct value.

The main sources of error in the second method are the every-day variations in photographic processing, the emulsion itself, the

temperature and especially humidity in the laboratory. All of these may, of course, be minimized by running the standards and unknowns on the same plate. Transmittances may then be compared visually and results will be accurate within $\pm 50\%$ of the amount present.

The techniques involved in squeezing out the optimum precision involve taking densitometric readings and plotting working curves. In this category, the simplest method is to plot % transmittance vs. % concentration on log-log paper. Alternatively, line-to-background ratios may be plotted with a significant gain in accuracy. Appropriate lines may be used for internal standardization.

Probably the most accurate technique devised to date, one truly quantitative and universal, is that of Tingle and Matocha.⁸ What they have done is to eliminate the known variables one by one until the desired accuracy—1 to 2% is claimed—is achieved. After the sample is pulverized to at least -100 mesh, and dried carefully, a 0.250g portion is mixed with 1.000g of lithium carbonate and 1.5000g of boric oxide. The mixture is then fluxed in a graphite crucible at 1000°C for 8 minutes. After solidifying, the resulting beads are ground in an impact grinder using a tungsten carbide vial and ball for about 1 minute. An automatic sieve shaker is used to remove 0.300g of -325 material and this is mixed mechanically with 0.600g of briquetting grade graphite powder which is screened for particle size uniformity, too. A $\frac{1}{2}$ " dia. pellet is made of the mixture using a hydraulic press at 44,000 psi. This is sparked and analyzed with a direct-reading spectrometer (Quantometer).

Though unwieldy and costly for the spectrographer with but an occasional sample to analyze, the method of Tingle and Matocha has been adopted by the Aluminum Company of America for routine analysis. Mechanization at almost every step has not only been rewarded with a fast method but one

dependable and highly accurate as well. It has been successfully tested not only on innumerable production samples but also by the National Bureau of Standards. The one drawback is in sensitivity where the dilution of the sample and the use of a spark limit the detectability to around 0.01% for the "average" element.

Because most methods of semiquantitative analysis lean so heavily on dilution, one obvious disadvantage involves sensitivity. If a sample contains an element at around its sensitivity level, a ten-fold dilution ordinarily drops the lines below the threshold of detectability. Especially in view of the current intense interest in trace elements, this problem is indeed significant.

How to improve sensitivity has been the subject of numerous recent papers, increasing emphasis being placed on the use of atmospheres excluding nitrogen.^{9, 10} Various concentrations of argon-oxygen appear to be the most common choice. While the actual improvement in limits of detection is too closely related to the individual spectrograph to be stipulated, it can be stated categorically that, for those elements with most persistent lines in the broad cyanogen band regions, there is at least a ten-fold improvement in sensitivity using a nitrogen-free atmosphere. The best means for achieving such an atmosphere is an enclosed chamber. A simpler means of reducing—but not entirely eliminating—nitrogen is with a Stallwood Jet.¹¹ The latter, operating in the open, uses a sheath of gas blowing concentrically upwards around the arc gap.¹²

REFERENCES

1. FRY, D. L., *A.S.T.M. Bulletin*, **216**, 29 (Sept. 1956).
2. SLAVIN, M., *Ind. Eng. Chem. (Anal. Ed.)*, **10**, 407 (1938).
3. HARVERY, C. E., "A Method of Semi-Quantitative Spectrographic Analysis," App. Res. Labs., Glendale, Calif. (1947).
4. MITTELDORF, A. J., AND LANDON, D. O., *App. Spec.*, **10**, 12 (1956).

5. HODGE, E. S., AND BAER, W. K., *App. Spec.*, **10**, 150 (1956).
6. JAYCOX, E. K., *Anal. Chem.*, **27**, 347 (1955).
7. WEAVER, J. R., AND BRATTAIN, R. W., *Anal. Chem.*, **21**, 1038 (1941).
8. TINGLE, W. H., AND MATOCHA, C. K., *Anal. Chem.*, **30**, 494 (1958).
9. RUPP, R. L., KLECAK, G. L., AND MORRISON, G. H., *Anal. Chem.*, **32**, 931 (1960).
10. OLDFIELD, J. H., AND BRIDGE, E. P., *The Analyst*, **85**, 97 (1960).
11. MITTELDORF, A. J., *The Spec Speaker*, **5**, No. 1, 6 (1960).
12. STALLWOOD, B. J., *J. Opt. Soc. Am.*, **44**, 172 (1954).

A. J. MITTELDORF

SILICON-GERMANIUM ALLOYS

The spectrograph is most generally used for analyses of minor or trace constituents. This is especially true in the electronics industry where scientists are constantly striving to obtain materials for semi-conductor use with impurities in the parts per billion range. For example, boron has been determined in silicon in this range.⁴ The graphite spark technique has also been developed for determining very small amounts of impurities in silicon and other semi-conductor materials.³

The spectrograph has also been useful in

the analyses of major constituents wherever chemical methods involve difficult separations or the methods are long and tedious. Two component systems have been analyzed over the entire concentration range by the spectrographic method. Raikhbaum⁵ studied the lead-tin system; Herman² studied the system niobium pentoxide-tantalum pentoxide; and Gardels and Whitaker¹ studied the silicon-germanium system.

In the analyses of silicon-germanium alloys it was found that this binary system could be analyzed over a concentration range of 1 to 98 mole % silicon by first using germanium as a variable internal standard for silicon and then using silicon as a variable internal standard for germanium. A total of only three silicon lines and one germanium line was used. The line pair Si-2506/Ge-2498 covered the 1 to 15 mole % silicon region and the pair Si-2435/Ge-2498 covered the 5 to 70 mole % silicon. For alloys of higher silicon content, silicon was used as the internal standard with the pair Ge-2498/Si-2535 being used for the analysis. With a d.c. arc procedure, the standard deviation was less than $\pm 8\%$ of the amount of the element being determined over a range of concentrations.

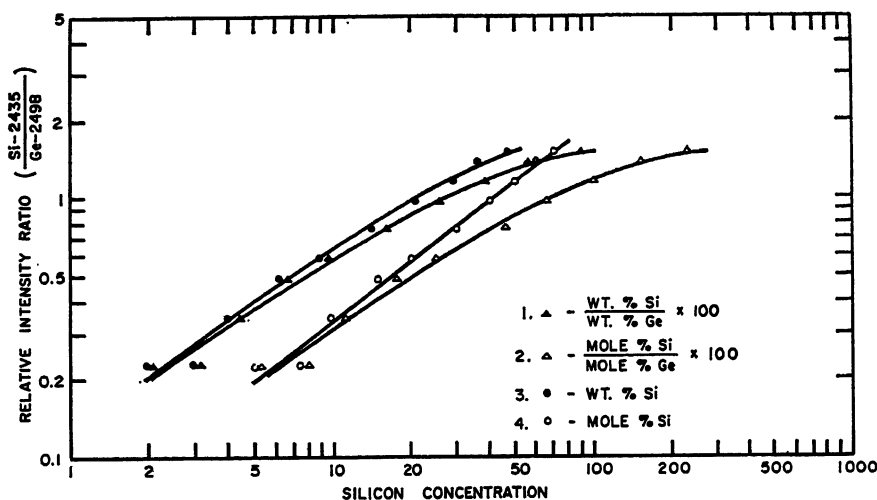


FIG. 1. Group of analytical curves for silicon.

The working curves were prepared by plotting mole % vs. the relative intensity ratio. This method of plotting gave a straight line calibration curve using a variable internal standard even though theory predicts that a straight line would be obtained when plotting concentration ratios vs. relative intensity ratios. Figure 1 illustrates the various methods of plotting concentrations for alloys containing 5 to 70 mole % silicon. The curvature of curves 1 and 2 towards the concentration axis indicates self absorption in the analysis line. The straight line obtained when plotting mole % is probably due to compensation for self absorption of the analysis line when a ratio plot is used. The wt. % plot would not be parallel to the mole % plot since wt. % silicon is not directly proportional to mole %. Curve 4 is convenient to use since it gives the answer directly and since the working curve is a straight line.

REFERENCES

1. GARDELS, M. C., AND WHITAKER, H. H., *Anal. Chem.*, **30**, 1496-1498 (1958).
2. HERMAN, H., *Spectrochim. Acta*, **3**, 389 (1948).
3. MORRIS, J. M., AND PINK, F. X., "Symposium on Spectrochemical Analysis For Trace Elements," pp. 39-46, ASTM Special Technical Publication No. 221, Philadelphia, Pa., 1957.
4. MORRISON, G. H., AND RUPP, R. L., *Anal. Chem.*, **29**, 892-895 (1957).
5. RAIKHBAUM, YA. D., *Zavodskaya Lab.*, **8**, 1101-5 (1939).

MARVIN C. GARDELS

SOLUTIONS, SPECTROCHEMICAL ANALYSIS OF

In recent years the use of solutions in spectrographic analysis has rapidly increased. This may be due to the problems posed by the development of new alloys, by the growing use of "new" metals, and by additional interest in fields hitherto considered unusual, such as analysis of trace elements in organic materials.

The use of solutions has numerous advantages. One is increased sensitivity. As an example, the application of ion-exchange meth-

ods for analysis of trace elements in organic materials has improved the sensitivity of spectrochemical methods by several orders of magnitude.

Another advantage is a saving in time. A simple, practical solution method can save the time ordinarily required to prepare a sample for analysis, as many samples submitted to the laboratory are already in the form of solutions. Additional time can be saved by analyzing an aliquot rather than the entire sample. For example, if the average value of the composition of a multitude of samples is to be determined, small portions of the components can usually be put in solution quite conveniently and an aliquot treated as the homogeneous average of the total.

Standard samples can be prepared at will to contain any concentration of the elements of interest.

Furthermore, solution analysis is often the simplest approach. Heterogeneous samples cannot be reasonably analyzed by a point-to-plane technique. This applies to metallic samples which form an excessively large grain structure upon solidification. Quantitative analysis of semiconductor and non-conductor materials can often be accomplished more readily and accurately by solution techniques as opposed to standard d.c. arc methods.

The only requisite for solution analysis is that the sample be indeed a true solution. Therefore, the chemistry of the sample must be considered carefully because precipitation of a component must be avoided.

The many outstanding advantages of solution techniques by far overshadow some of the objections. Newer and simpler methods have become available which make most of the procedures easier, faster, and more convenient, and eliminate to a large extent the spattering which has so often been associated with solution methods. Solution analysis often remains the only practical approach to the solution of an analytical problem.

Methods

For convenience, solution methods can be classed into four general categories:

(1) Spray methods. The solution is sprayed into the discharge gap by means of a pressure system or by means of reduced pressure in the discharge gap.

(2) Capillary-action systems. The solution is brought to the discharge gap by capillary action.

(3) Mechanical devices. The solution is brought to the discharge gap by a mechanical device.

(4) Evaporation and absorption techniques. The solution is evaporated on or absorbed by a matrix (electrode) material and thus brought to the discharge.

Spray Methods. Although classical flame photometry properly belongs to this classification, it is discussed elsewhere (p. 330) because it is usually treated as an independent analytical method.

The method of Eberius¹ is a clean method though somewhat wasteful of sample material (Fig. 1). It utilizes two drilled graphite stick electrodes of 5-mm diameter. The upper one has a 3-mm hole and the lower one a 1.5-mm hole. The sample is contained in a leveling container which is connected to the

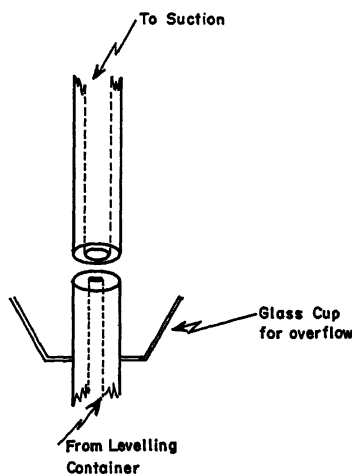


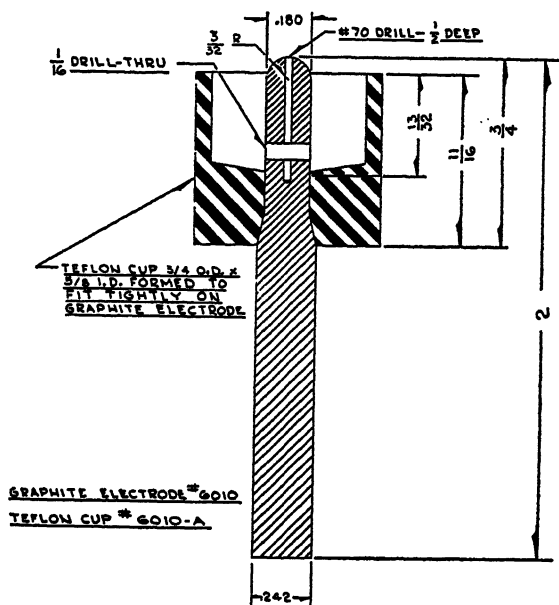
FIG. 1. Eberius method.

lower electrode by tubing. In this manner the sample flows through the electrode into the gap. The upper electrode is connected by tubing to a water suction device which removes droplets and excess vapors from the excitation gap and, secondarily, assists in the maintenance of a continuous flow of material to the gap. A glass collar is attached to the lower electrode to collect that portion of waste solution which drops from the gap and is not removed by the suction at the counter electrode.

Another method, by DuBois, Tuteur, and Mahan,² is based on a series of atomizing devices which discharge into a plastic container. The vapors produced are forced through a drilled electrode which is attached to the top of the container. A graphite stick electrode serves as the counter electrode. Varying the pressure and the nozzle size of the vaporizers adjusts the amount and the density of the solution presented to the gap.

In the vacuum-cup electrode method (Fig. 2), Zink³ uses the reduced pressures which are normally present in the discharge gap to transport the sample from a reservoir to the gap. There it appears as a fine spray and is vaporized and excited. Using an a.c. discharge, he utilizes, in effect, a pump. The pressure in the gap fluctuates with each half-cycle and the speed of pumping is regulated by the number of discharges per half cycle. As an alternative, Zink proposes a $2\frac{1}{4}$ inch-long graphite rod drilled with a No. 70 drill. By means of this rod, the same reduced-pressure pump system transports the sample to the gap. An advantage of this variation is that the sample can be taken directly from the beaker in which it was prepared, and thus the chances for contamination are reduced. The sensitivity is higher than that of many methods by several orders of magnitude, with no loss of precision.

The "spark-in spray" technique of Malmstadt and Scholz,⁴ also utilizes spark excitation. A Beckman burner is used as in the normal flame method, but the less easily ex-



(Courtesy of United Carbon Products Co., Bay City, Michigan)

FIG. 2. The "vacuum-cup" electrode.

cited elements are volatilized and excited by a spark, which is made to break down across the very fine spray produced by the atomizer.

The application of the plasma jet to spectrochemical analysis is described by Margoshes and Scribner.⁵ There is no doubt that the application of a relatively low current (15–20 A) plasma jet, which can be driven by most presently existing d.c. arc sources, will prove to be a boon to spectrography.

Capillary-Action Systems. Various methods based on capillary action are found in the literature. Twyman⁶ mentions the method of Hartley,⁷ which may function at least in part by capillary action. Since the time of Hartley's work, many other capillary methods have been developed. None, however, have become very successful.

Hartley introduces his sample into a glass U tube. One end is stoppered with a "brush" which is cut from "good" graphite and which is connected to the excitation source, a Leyden jar, by a platinum wire. Similarly, the

counter electrode is a graphite brush held in a glass tube and connected by a platinum wire.

One of the more successful methods is the "plastic cup" method (Fig. 3) of Henry and

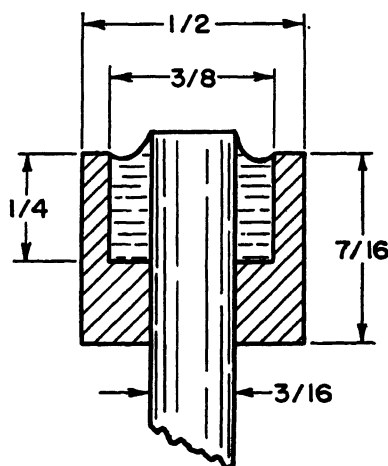


FIG. 3. The "plastic cup" electrode configuration. The "Lucite" cup is attached to the graphite electrode by means of "Duco" cement.

Leslie.⁸ A simple, straightforward method, it employs "capillary action" along the electrode surface to transport the sample to the electrode top for excitation. The tendency of the solution to boil under more severe excitation conditions enhances this action.

A variation of this method is described by Mitchell, Orme, and Farrell.¹⁰ The cup is made of glass in the shape of a small funnel. The electrical connection is made by means of a tungsten wire which is fused into the funnel. A cap of graphite placed over the upper end of the tungsten wire provides the counter electrode and the medium for capillary action.

Eichhoff's capillary electrode (Fig. 4) was used as the basis for the vacuum-cup electrode.³ While it is somewhat cumbersome, it is a useful method when only a small amount of sample is available.¹¹⁻¹²

Mechanical Devices. Most of the presently used techniques apply some mechanical means of transporting the sample to the analytical gap. The most favored of these

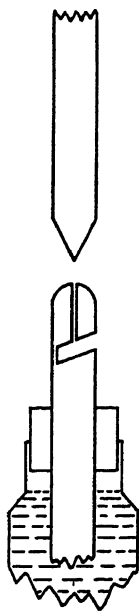
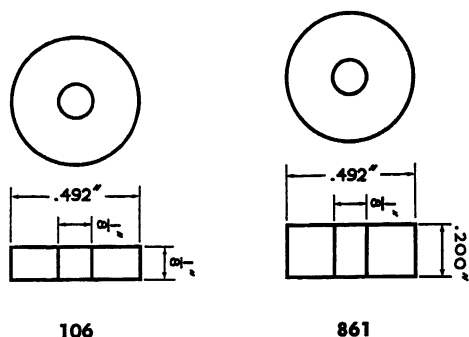
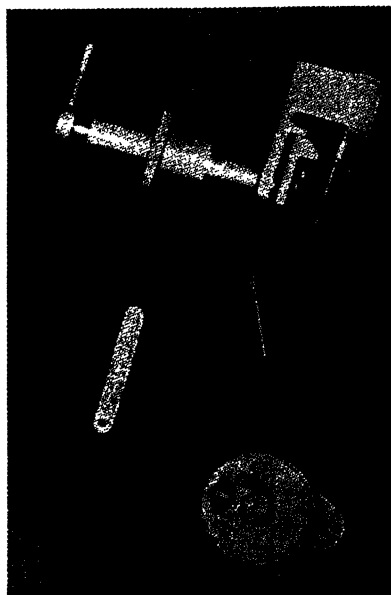


FIG. 4. The capillary electrode by Eichhoff.



(Courtesy United Carbon Products Company)

(a)



(Courtesy Jarrell-Ash Company)

(b)

FIG. 5. (a) Preformed rotating electrode disks. (b) Rotating electrode attachment.

is the rotating-disk electrode¹³⁻²¹ (Fig. 5) generally credited to Pagliassotti and Porsche.¹³ Although it was originally developed for analysis of petroleum products, its use has been extended to many solution problems. A graphite disk is attached to a shaft driven by a small electric motor. The various speeds that have been recommended appear to depend upon the speed of the motor available. Many investigators claim that the speed is of

of little consequence as long as it remains between 5 and 25 rpm. Most investigators agree, however, that the speed, once selected, must be maintained, since variations of the rate of rotation tend to exert an influence on the slope of the working curves. Drastic changes in the temperature of the sample also tend to vary the spectral intensity. The disk is located directly below the counter electrode and is separated from it by an appropriate gap, usually 2 or 3 mm. The lower portion of the disk dips into the solution, which is contained in a small aluminum or porcelain boat. Thus new sample solution is presented to the analytical gap continuously.

Sventitskij²¹ used a copper disk in a similar arrangement for determination of halogens and sulfur.

Bardocz²² reports that his variation of this scheme produces better accuracy and reproducibility (Fig. 6a and b). The rotation of the electrodes is synchronized to the discharges of the electronically controlled source units to improve accuracy and reproducibility. Another advantage of this system is that the drop of solution held on the electrode is almost completely consumed. The number of revolutions per minute is the decisive factor.

A mechanical device is also used in the Platrode electrode²³ system of Rozsa and Zeeb (Fig. 7). The sample is evaporated on the horizontally rotating disk. The disk rotates slowly, at 5–15 rpm, under the counter electrode. This method, too, was originally devised for analysis of petroleum products and the determination of wear elements in lubricating oils, but it has since found considerable application to solution analysis. It is also applicable when the sample is not a true solution, i.e., when the suspended particles are small enough to remain in suspension long enough to transfer the sample to the electrode.

The porous-cup electrode of Feldman²⁴ is one of the most favored techniques (Fig. 8). A $\frac{1}{4}$ -inch-diameter electrode is drilled precisely to produce a cup with an extremely

thin bottom. The solution is permitted to seep through the porous graphite and is excited by the discharge between the porous cup and the counter electrode placed beneath it. Because the porous cup is an excellent filter, it cannot be used for analysis of materials in suspension. Some investigators have found that it is helpful to pre-arc the cup in order to improve its porosity. In some applications coating the outside of the cup with lacquer or other sealing material, such as Fisher's Label Glaze,²⁴ prevents seepage through the sides and damage to the electrode jaws. One problem involved in this technique is that only relatively mild excitation parameters can be used, since the solution escapes from the cup if it is brought to the boiling point. Cooling of the electrode jaws by water is of questionable value because the relatively low heat conductivity of graphite hinders rapid dissipation of heat. Another problem is that fractionation by adsorption may occur as the sample passes through the hot graphite. Despite these problems, excellent results have been reported by many investigators using this method.²⁴⁻²⁶

Evaporation and Absorption Techniques. More ingenuity has been applied in this category than in any of the others. The reason for this may be that this type of system is more closely allied to normal wet chemical processes and therefore more familiar to every chemist. Filter papers and all kinds of materials have been impregnated with samples and exposed in one manner or another. Some of the more outstanding methods are the following.

The straight cut-top electrode procedures are the oldest and probably the most commonly used. Particularly when the solution sample is limited to a few tenths or even a few hundredths of a milliliter, these methods are very valuable. Wilhelm²⁸ recommends that the electrode be coated with a thin layer of paraffin or mineral oil, prior to application of the sample, to prevent partial

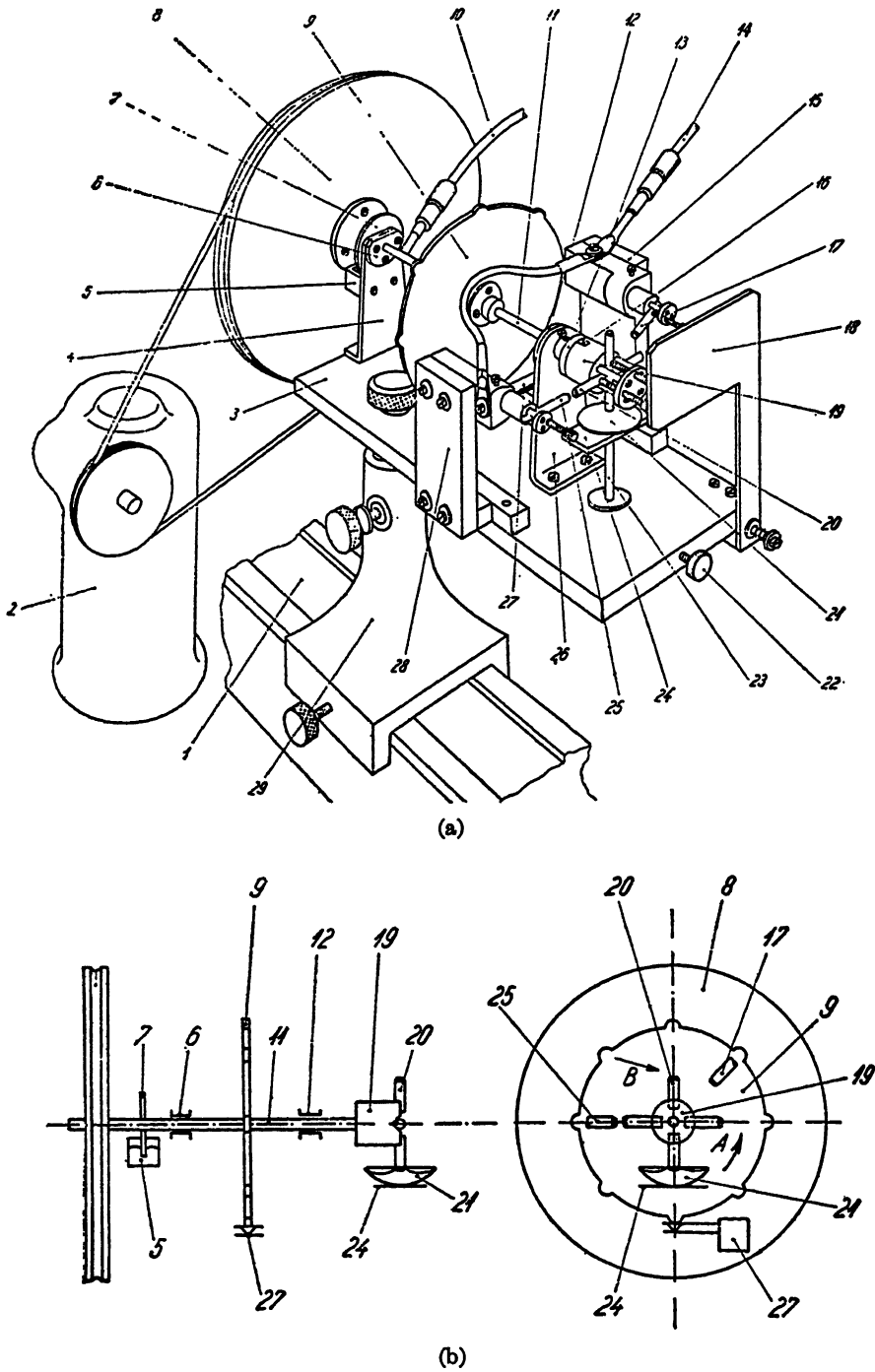
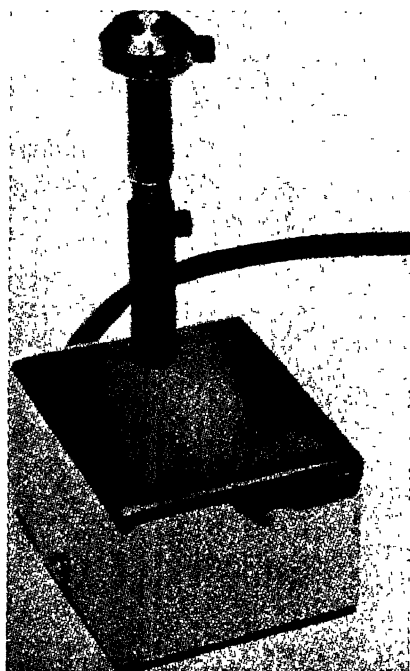
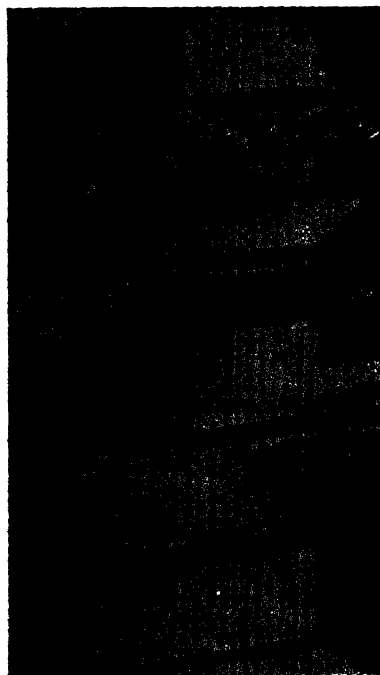


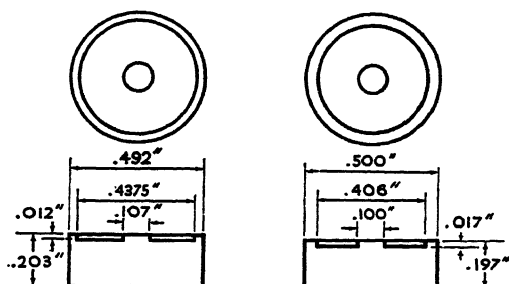
FIG. 6. (a) The Bardocz variation to the rotating electrode. The electrode dips into the dish (21), and is exposed against the counter electrode (25). (b) Detail of the Bardocz configuration showing pre-arc electrode (17).



(Courtesy National Spectrographic Laboratories)
(a)



(Courtesy National Spectrographic Laboratories)
(b)



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(Courtesy United Carbon Products Company)

(c)

FIG. 7. (a) A Platrode electrode attachment.
(b) A Platrode attachment in the excitation stand.
(c) Preformed shapes-Platrode electrodes.

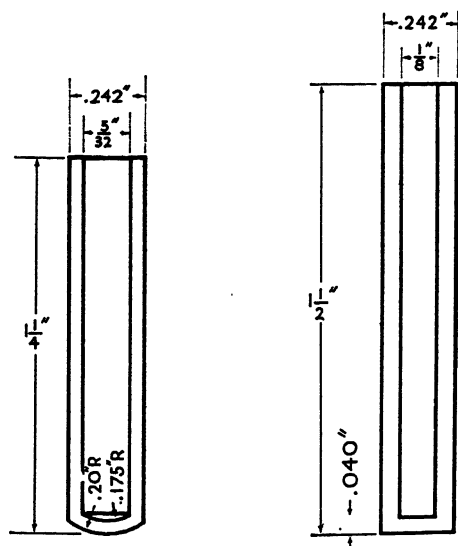
absorption of the sample by relatively porous graphite electrodes. The same technique has also been used successfully with Platrode electrodes.

When a larger sample is available, the method of Scheibe and Rivas³⁶⁻³⁷ is suitable. They recommend that the sample be applied to and evaporated upon a graphite electrode made porous by heating in a d.c. arc. This allows more sample to be deposited, and a longer and more sensitive exposure can be made.

A modification of their method was suggested by Mathis,³⁸ who drilled a small hole into the top of the flat-top electrode and placed powdered graphite in it. The powder was impregnated with the sample, and the sample was blown into the gap under excitation by a spark.

Not only graphite is used for flat-top electrodes. Gerlach and Riedl³⁹ used a highly polished copper surface for evaporation of the sample. Fred⁴⁰ and his colleagues obtained excellent results with this method. The solution to be used should be diluted to a considerable extent to avoid formation of a crust, as a crust tends to be ejected from the electrode by the impact of the first discharge.⁴¹⁻⁴²

For determination of traces of copper,

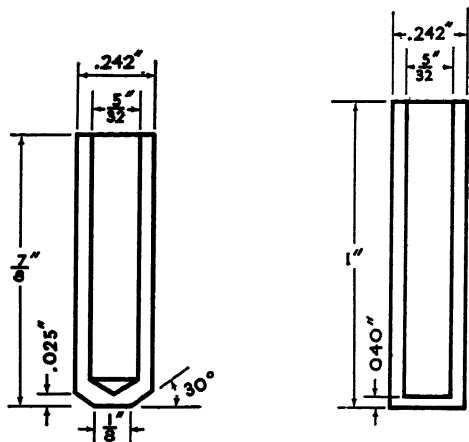


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(Courtesy United Carbon Products Company)

(a)



204

910

(Courtesy United Carbon Products Company)

(b)

FIG. 8. (a) Preformed shapes—porous-cup electrodes. (b) Preformed shapes—porous-cup electrodes.

Mann⁴⁸ as well as Mayer and Holik⁴⁴ used aluminum rods which were made slightly porous by anodizing or etching with acid. Elimination of most of the cyanogen bands

by the use of metal electrodes is a welcome adjunct to these methods. It is primarily the ease of handling which accounts for the popularity of graphite electrodes.

Bruening's method⁴⁵ is exact though somewhat involved for routine analytical work. A mixture of suitable metal powder, such as silver, copper, or aluminum, and an organic material, such as anthracene, is used. The mixture is pressed as a thin layer upon a rod of electrode material, and the anthracene is evaporated. A spongelike form of metal remains which consists of approximately 90% pores. The sample solution is absorbed by this sponge. A considerable amount of the sample can be evaporated on the large surface area of the sponge and can be excited by any of the excitation parameters available with today's sources. The lines emitted by the metal of the sponge are conveniently used as reference lines.

For the analysis of oils and similar materials. Calkins and White⁴⁶⁻⁴⁷ recommend the use of a graphite electrode heated to a red glow and then quenched in the sample. In this manner the electrode absorbs a quantity of sample material and is used as the lower electrode in the discharge.

In a method suggested by Svejda,⁴⁸ the sample is placed as a solution into a shallow dished area on a flat, round metal electrode (Fig. 9). The electrode is held in a support on a deGramont excitation stand and arced or sparked. Additional methods of interest are in the literature.⁴⁹⁻⁵¹

Conclusion

All too often a method which is unsuccessful as applied to one problem is excellent for another. As in most of analytical chemistry, there is not now and there is unlikely to be a universal method equally useful for the solution of all problems.

The application of solution techniques has found increasing favor among analytical emission spectroscopists in the past few years. These techniques not only lessen the

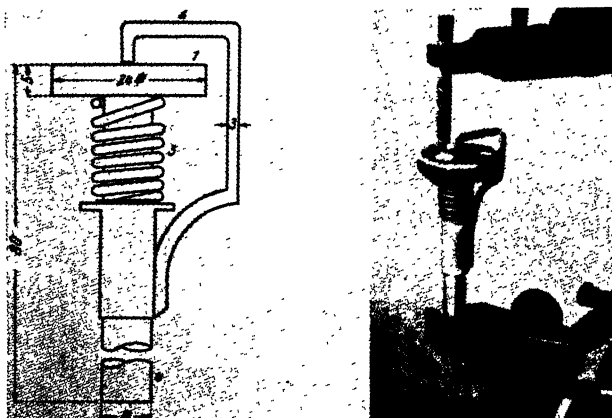


FIG. 9. The dished disk electrode configuration according to Svejda.

standardization problem but also increase the sensitivity of analysis in many instances. Ion exchange techniques, in particular, have aided in increasing sensitivity.

A bibliography is included to acquaint the reader with the less well-known methods. Some of these could also serve as basis for new methods to resolve some of the pressing problems in today's laboratory.

REFERENCES

1. EBERIUS, E., *Trans. Coll. Spect. Int.* IV (1953).
2. DuBOIS, E. M., TUTEUR, A., AND MEHAN, J. L., Wright Air Development Center, WADC-TR-55-108.
3. ZINK, T. H., *Appl. Spectroscopy*, **13**, 4 (1959).
4. MALMSTADT, H. V., AND SCHOLZ, R. G., *Anal. Chem.*, **27**, 881 (1955).
5. MARGOSHEE, M., AND SCRIBNER, B. F., *Spectrochim. Acta*, **138** (1959).
6. TWYMAN, F., "The Spectrochemical Analysis of Metals and Alloys," Chemical Publishing Co., Inc., New York, 1941.
7. HARTLEY, W. N., *J. Chem. Soc.*, **41**, 90 (1882).
8. HENRY, W. M., AND LESLIE, E., Batelle Memorial Inst., Columbus, O. Unpublished.
9. FRED, M., AND CORVIN, I., unpublished. Cited in reference 24.
10. MITCHELL, G. P., ORME, G., AND FARRELL, F., *Spectrochim. Acta*, **272** (1959).
11. EICHHOFF, H. J., AND PICARD, K., *Spectrochim. Acta*, **7**, 396 (1955-6).
12. EWLES, J., AND CURRY, C., *Proc. Leeds Phil. Lit. Soc.*, **4**, 299 (1946).
13. PAGLIASOTTI, T. P., AND PORSCHKE, F. W., *Anal. Chem.*, **23**, 198 (1951).
14. PAGLIASOTTI, T. P., AND PORSCHKE, F. W., *Anal. Chem.*, **23**, 1829 (1951).
15. PAGLIASOTTI, T. P., AND PORSCHKE, F. W., *Anal. Chem.*, **24**, 1408 (1952).
16. PIERUCCI, M., AND BARBANTI-SILVA, L., *Nuovo Cimento*, **17**, 275 (1940).
17. WELSBACH, FRH. AUER, V., *Monatshefte*, **43**, 387 (1922).
18. SMITH, R. G., BOYLE, A. J., FREDERICK, W. G., AND ZAK, B., *Anal. Chem.*, **24**, 406 (1952).
19. HELLER, H. A., AND LEWIS, R. W., *Anal. Chem.*, **25**, 1038 (1953).
20. MOSHER, R. E., *Anal. Chem.*, **23**, 1514 (1951).
21. SVENITSKIJ, N. S., *J. Tech. Phys. U.S.S.R.*, **14**, 605 (1944).
22. BARDOZ, A., AND VARSANYI, F., *Acta Chim. Hung.*, **7**, 1 (1955).
23. ROZSA, J. T., AND ZEEB, L. E., *Petroleum Processing*, **8**, 1708 (1953).
24. FELDMAN, C., *Anal. Chem.*, **21**, 1041 (1949).
25. CLINTON, O. E., *Spectrochim. Acta*, **286** (1959).
26. FELDMAN, C., HAWKINS, M. B., MURRAY, M., AND WARD, D. R., *Anal. Chem.*, **22**, 1400 (1950).
27. OWEN, L. E., AND ELLENBURG, J. Y., *Anal. Chem.*, **23**, 1823 (1951).
28. NORRIS, J. A., AND PEPPER, C. E., *Anal. Chem.*, **14**, 1399 (1952).
29. GAMBRILL, C. W., GASSEMAN, A. G., AND O'NEILL, W. R., *Anal. Chem.*, **23**, 1365 (1951).
30. DIXON, D., *Trans. Coll. Spect. Int.* IV, Münster (1953).
31. AYRES, G. H., AND BERG, E. W., *Anal. Chem.*, **24**, 465 (1952).
32. HYMAN, H. M., *Appl. Spectroscopy*, **12**, 95 (1958).

33. MITCHELL, R. L., AND SCOTT, R. O., *Appl. Spectroscopy*, **11**, 6 (1957).
34. SLAVIN, M., personal communication.
35. WILHELM, H. A., *Ind. Eng. Chem. (Anal. Ed.)*, **10**, 211 (1938).
36. SCHEIBE, G., AND RIVAS, A., *Z. angew. Chem.*, **49**, 443 (1953).
37. SLOVITER, H. A., AND SITKIN, A., *J. Opt. Soc. Am.*, **34**, 400 (1944).
38. MATHIS, W. T., *Anal. Chem.*, **25**, 943 (1953).
39. GERLACH, W., AND RIEDL, E., *Z. anorg. Chem.*, **103** (1934).
40. FRED, M., NACHTRIEB, N. H., AND TOMKINS, F. S., *J. Opt. Soc. Am.*, **32**, 279 (1947).
41. FARIS, F. P., *Appl. Spectroscopy*, **12**, 157 (1958).
42. NACHTRIEB, N. H., "Principles and Practice of Spectrochemical Analysis," p. 272, McGraw-Hill Book Co., Inc., 1950.
43. MANN, K. E., *Spectrochim. Acta*, **1**, 560 (1941).
44. MAYER, F. X., AND HOLIK, L., *Spectrochim. Acta*, **4**, 218 (1950).
45. BRUENING, F. J., *Trans. Coll. Spect. Int. IV*, Münster (1953).
46. CALKINS, L. E., AND WHITE, M. M., *Natl. Petroleum News*, **38**, 519 (1946).
47. CLARK, O. R., *Anal. Chem.*, **23**, 1348 (1951).
48. SVEJDA, H., *Microchim. Acta*, **251** (1955).
49. JOLIBOIS, P., AND BOSSINET, R., *Compt. rend.*, **302**, 400 (1936).
50. TWYMAN, F., AND HITCHEN, C. S., *Proc. Roy. Soc. London*, **A133**, 72 (1931).
51. GERLACH, W., AND SCHWEITZER, E., "Die Chemische Spektralanalyse der Elemente, I" Leopold Voss, Leipzig, 1933.
- FREDERICKSON, L. D., *Appl. Spectroscopy*, **7**, 19 (1953).
- FRY, D. L., *Appl. Spectroscopy*, **10**, 65 (1956).
- GASSMANN, A. G., AND O'NEILL, W. R., *Anal. Chem.*, **21**, 417 (1949).
- GILLIS, J., AND EECKHOUT, J., *Anal. Chem. Acta*, **1**, 377 (1947).
- GILLIS, J., AND EECKHOUT, J., *XI Congr. G.A. M.S.*, **51** (1949).
- GILLIS, J., AND EECKHOUT, J., *Silicates Industriels*, **15**, 213 (1950).
- HANSEN, J., *Anal. Chem.*, **23**, 1362 (1951).
- HITCHCOCK, R. D., AND STARR, W. L., *Appl. Spectroscopy*, **8**, 5 (1954).
- HULLINGS, R. S., *Appl. Spectroscopy*, **12**, 139 (1958).
- KEIRS, R. J., AND ENGLIS, D. T., *Ind. Eng. Chem. (Anal. Ed.)*, **12**, 275 (1940).
- LAUENSTEIN, A., *Metallwirtschaft*, **22**, 318 (1943).
- LAMB, F. W., *Ind. Eng. Chem. (Anal. Ed.)*, **12**, 275 (1940).
- LUNDEGÅRD, H., "Die quantitative Spektralanalyse der Elemente," Gustav Fischer, Jena, 1929.
- MEGGERS, W. F., AND SCRIBNER, B. F., "Index to the Literature on Spectro-Chemical Analysis," I, II, III, 1941, 1947, 1954, A.S.T.M., Philadelphia.
- PAYLOVSKI, G., AND MAVRODINEANU, R., *Bull. Soc. Roum. Phys.*, **42**, 53 (1941).
- PETERSON, M. F., *Anal. Chem.*, **22**, 1398 (1950).
- PFEILSTICKER, K., *Spectrochim. Acta*, **4**, 100 (1950).
- RIVAS, A., *Z. angew. Chem.*, **50**, 903 (1937).
- ROHNER, F., *Helv. Chim. Acta*, **20**, 1054 (1937).
- ROUIR, E. V., AND VANBOKESTAL, A. M., *Spectrochim. Acta*, **4**, 330 (1951).
- RUEHLE, A. E., AND JAYCOX, E. K., *Ind. Eng. Chem. (Anal. Ed.)*, **12**, 260 (1940).
- SALTMAN, W. M., AND NACHTRIEB, N. H., *Anal. Chem.*, **23**, 1503 (1951).
- SCRIBNER, B. F., AND BALLINGER, J. C., *Anal. Chem.*, **22**, 508 (1950).
- SCRIBNER, B. F., AND BALLINGER, J. C., *J. Research NBS*, **47**, 221 (1951).
- SLOVITER, H. A., AND SITKIN, A., *J. Opt. Soc. Am.*, **34**, 400 (1944).
- SMITH, J. L., YAEGER, E., KAUFMAN, N., AND HOVORKA, F., *Anal. Chem.*, **23**, 1721 (1951).
- STECHE, R. M., BEDELL, H. M., AND LEWIS, I., *J. Lab. Clin. Med.*, **34**, 616 (1949).
- THOMSON, K. B., AND DUFFENDACK, O. S., *Phys. Rev.*, **49**, 880 (1936).
- TÖRÖK, T., AND SZAKACS, O., *Acta Chim. Hung.*, **3**, 413 (1953).
- UZUMASA, Y., AND OKUNO, H., *J. Chem. Soc. Japan*, **56**, 1174 (1935).

BIBLIOGRAPHY

APPLIED RESEARCH LABORATORIES, *Spectrographers Newsletter*, **2**(9) (1948); **2**(10) (1949); **5**(1) (1953).

BAUER, R., *Aluminium*, **2**(9) (1940).

CHOLAK, J., AND STORY, R. V., *J. Opt. Soc. Am.*, **31**, 730 (1941).

CONWAY, J. G., AND MOORE, M. F., *Anal. Chem.*, **24**, 610 (1952).

DELANEY, J. C., AND OWEN, L. E., *Anal. Chem.*, **23**, 577 (1951).

VAN DOORSELAER, J., EECKHOUT, J., AND GILLIS, J., *XII Congr. G.A.M.S.*, **51** (1949).

DUFFENDACK, O. S., AND WOLFE, R. A., *Proc. Fifth Summer Conf. on Spectroscopy*, John Wiley and Sons, 1938.

ELLS, V. R., *J. Opt. Soc. Am.*, **31**, 534 (1941).

ERRERA, J., *Compt. rend.*, **176**, 1874 (1923).

FAST, E., AND NIELSON, J. R., *J. Opt. Soc. Am.*, **37**, 614 (1947).

VAN SOMEREN, E. H. S., AND LADIMANN, F., *Spectrochem. abs. IV*, Hilger and Watts, Ltd., London, 1955.

WHITEHEAD, T., AND WILLIAMS, E. W., *Ind. Eng. Chem. (Anal. Ed.)*, 17, 490 (1945).

YOUNG, L. G., AND BERRIMAN, J. M., *Nature*, 166, 435 (1950).

THEODORE H. ZINK

SOURCE-EFFECTS ON ACCURACY. See ACCURACY IN SPECTROCHEMICAL ANALYSIS, p. 99.

SPECIAL TECHNIQUES BY U.S. GEOLOGICAL SURVEY

Rare Earths and Thorium in Phosphate Rock¹

In laboratory investigations, interest developed in the possible rare-earth content of phosphate samples from Florida and the northwestern United States. Because of the difficulty of making chemical determinations of traces of individual rare earths, a combined chemical-spectrographic method was investigated. After removal of iron by the extraction of the chloride with ether, the rare earths and thorium are concentrated by double oxalate precipitation, using calcium as a carrier. The rare earths are freed from calcium by an ammonium hydroxide precipitation with a fixed amount of aluminum as a carrier. The aluminum also serves as an internal standard in the final spectrographic analysis. The method will determine from 0.02 to 2 mg. of each rare earth with an error no greater than 10%. The investigation has resulted in a fairly rapid and precise procedure, involving no special spectrographic setup. The method could be applied to other types of geologic materials with the same expected accuracy.

Semiquantitative Analysis of Minerals, Rocks and Ores²

The quantity and complex nature of materials received for analysis in the spectrographic laboratories of the U. S. Geological

Survey have emphasized the need for a spectrographic method to determine a maximum number of elements in a limited time with a reasonable degree of accuracy. The semi-quantitative method described determines 68 elements in one arcing of 10-mg. sample. The method has been used to complete 245,000 determinations during a 3-year period. Each determination is reported as a concentration range or bracket (0.001 to 0.01, 0.01 to 0.1%, etc.). A chemical check of 500 such determinations showed 92% in agreement; the remaining 8% agreed to within one bracket. The method requires a minimum of sample handling, thus reducing the chances of contamination, detects low concentrations of elements, and is rapid. Analyses have been completed on a wide variety of materials.

Germanium in Low-Rank Coal³

The U. S. Geological Survey is currently investigating radioactive lignites and low-rank coal on behalf of the Atomic Energy Commission. As part of this study, many hundreds of samples of ashed low-rank coals are analyzed spectrographically by semi-quantitative methods for a total of 69 elements. Germanium is one of the elements of prime importance as a possible by-product in any processes that may be developed to extract uranium from low-rank coal.

Natural low-rank coal samples, ground to -80 mesh, are ashed at temperatures exceeding 500° C in preparation for spectrographic analysis. The question arises whether germanium is lost by volatilization during ashing and therefore would be undetected in the spectrographic analysis even if present in the sample before ashing. The tests included gradual heating, rapid heating, and increased surface area effects. All indicated no loss of germanium as shown in Table 1.

Selenium, Analysis of⁴

Selenium can be determined in pyrite, chalcocite, and marcasite by a simple and rapid spectrochemical method that requires

EMISSION SPECTROSCOPY—LIGHT

TABLE 1. SPECTROGRAPHIC DETERMINATION OF GERMANIUM ON LOW-RANK COAL SAMPLES

Sample	Ashing Temp., °C.	Ashing Time, Hr.	Ash, %	Ge in Ash, % ^a (Spectro-graphic)
Gradual Heating of Samples				
R	200	4	68.80	— ^b
R	500	4	3.90	1.10
R	800	4	3.87	1.12
R	1000	2	3.80	1.12
O	200	4	99.94	— ^b
O	500	4	1.26	0.010
O	800	4	1.17	0.013
O	1000	2	1.28	0.012
E	200	4	85.44	— ^b
E	400	4	6.71	0.60
E	500	4	6.78	0.60
E	800	4	6.70	0.60
E	1000	2	6.62	0.55
Rapid Heating of Samples				
R	800	4	3.83	1.10
O	800	4	1.09	0.010
E	800	4	6.66	0.59
Rapid Heating of Samples in Wide Platinum Dishes				
R	1000	1	3.70	1.13
O	1000	1	1.28	0.012
E	1000	1	6.62	0.62
Rapid Heating of Samples in J. L. Smith Crucibles (Small Surface Area)				
R	1000	2	3.70	1.10
O	1000	2	1.28	0.012
E	1000	2	6.62	0.61

^a Calculated on basis of ash prepared at 500°C.

^b No spectrographic germanium results obtained, owing to high organic content remaining in sample.

no complicated arrangement of spectrographic equipment or chemical pretreatment of samples. Advantage is taken of the new short wave length radiation plates (Eastman) and the addition of copper oxide to enhance the selenium lines 2039.85 and 2062.78 Å. The possibility exists of determin-

ing many other elements on the same exposure of the sample. The method is applicable in the range of 0.0015 to 2% selenium. Tests indicate an average difference from the chemical results of 0.07% in the few per cent range, 0.03% in the 0.1 to 1.0% range, 0.005% in the 0.01 to 0.1% range, and 0.00075% in the 0.001 to 0.01% range. The relative accuracy over the entire range is to about 7% of the concentration.

REFERENCES

1. WARING, C. L., AND MELA, H., JR., *Anal. Chem.*, **25**, 432 (1953).
2. WARING, C. L., AND ANNELL, C. S., *Anal. Chem.*, **25**, 1174 (1953).
3. WARING, C. L., AND TUCKER, W. P., *Anal. Chem.*, **26**, 1198 (1954).
4. WARING, C. L., WORTHING, HELEN W., AND HAZEL, KATHERINE V., *Anal. Chem.*, **30**, 1504 (1958).

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TRACE ELEMENTS, SPECTROCHEMICAL ANALYSIS FOR

Sample Size Unlimited

Introduction. In trace-element analysis, the major problem confronting the spectrographer is how he can obtain the maximum sensitivity with his instrumentation. He strives to record spectral lines of elements, the total weight of which may be as little as 0.01 gamma. And neither are his efforts of academic interest alone. For trace-element problems are important in metallurgy where 0.0005% of boron will improve the hardenability of steel; in agriculture where a few ppm of cobalt in the soil are vital to the health of grazing animals; in electronics where the performance of a transistor is poisoned by the presence of less than 1 ppm of many elements; in phosphor manufacture where a trace of copper activates zinc sulfide; in geology where the presence of minute concentrations of elements in rivers guides scientists to deposits of those elements; in semi-quantitative spectrochemical analysis where

the sample is diluted so that its constituents are reduced to traces.

The examples given have one point in common: the sample is large or unlimited in size. But, equally important are problems involving a few mg or less of a sample. The composition of the deposit on an electrical contact may reveal the reason for the failure of that contact. The analysis of a microscopic inclusion may disclose the source of the inclusion. The term gaining favor for the latter is "microanalysis" as distinguished from "trace analysis."

To the spectrographer, the problems of the unlimited and limited sample have points in common. But they also differ considerably. The latter is one in which speed and sensitivity are closely akin. There is so little sample that the spectrum must be recorded before it vanishes from the electrode. In analyzing samples of unlimited size, on the other hand, speed is of little concern. The spectrographer can always use more sample and superimpose spectra if further registry of spectral lines is needed.

Spectrograph. With the unlimited sample on hand, the first question is which spectrograph to use if more than one is available; how to use the spectrograph if but one is in the laboratory. Here the primary consideration is dispersion. Many investigators have shown that sensitivity is directly related to dispersion. The sensitivity of any measurement corresponds to a signal-to-noise ratio. Translated into spectrographic terms, sensitivity is a line-to-background ratio. In an instrument of low dispersion, the background behind a line is concentrated. In one with large dispersion, the same background is spread out over a large area. The line itself in both spectrographs, being an image of the slit, remains the same width. Greater dispersion is thus responsible for lower background, a greater signal-to-noise ratio and, in turn, better sensitivity.

In "Practical Spectroscopy,"¹ Harrison, Lord and Loofbourow cite a beautiful ex-

ample of how dispersion and sensitivity are so intimately related. Using a 35-ft. spectrograph, ten tin lines could be photographed in a certain sample. With a medium quartz instrument, no tin lines appeared from the same sample, regardless of the exposure time.

In general, anything that improves the *effective* dispersion of a spectrograph will improve sensitivity. A grating spectrograph, for example, should be used at its highest useful order. Of course, *effective* dispersion should be emphasized. In the Ebert spectrographs, it is possible to utilize the 14th and even higher orders. Because of optical aberrations, pressure broadening of lines and many other factors, no gain in sensitivity will be noted beyond perhaps the 8th or 9th orders. With a prism instrument, it will often be found that a line in the short (high dispersion) wavelength region will be more sensitive than one at a longer wavelength, despite the handbook listings to the contrary.

Resolution is another important consideration in achieving optimum sensitivity. A weak, well-resolved line may just appear above its background while one poorly re-

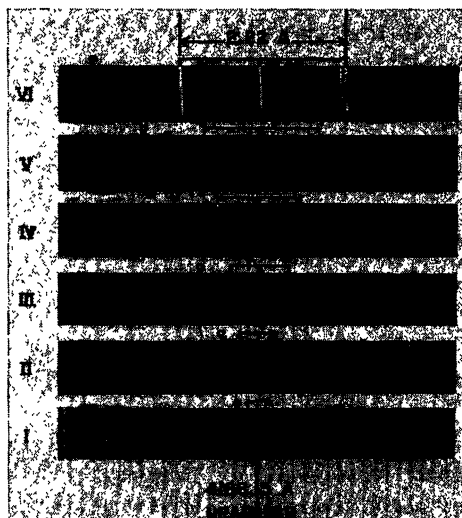


FIG. 1. Enhancement of sensitivity with increasing order and dispersion. Note the uranium 4188A group of lines and its increasing signal-to-noise ratio from order I to order VI.

solved will dissolve into the background. Basically illumination is the factor to contend with here. There is a direct relationship among illumination, resolution and sensitivity. Maximum resolution of any optical instrument is attained when its optics are just filled with light. Applied to a spectrograph, the illuminating system which just fills the grating or prism will result in the best resolution. External optics are so arranged that an image of the source is obtained on the entire height of the grating or prism collimator.

Now resolution is a horizontal affair, involving the width but not the length of a line. Its vertical counterpart is astigmatism or, rather, the lack of astigmatism. Just as a poorly resolved line is spread out horizontally, so an astigmatic line is spread out vertically. The effect is the same: a sacrifice of line intensity and consequent loss of sensitivity. Many grating and most prism spectrographs are stigmatic over wide wavelength intervals and so the effect does not apply to them. With instruments that suffer from astigmatism, it is often possible to so set the external optics that there is a limited wavelength region where the images are stigmatic. These settings should be made for the region of interest.

While on the subject of the slit, the question is often asked, what is the optimum slit width for the highest signal-to-noise ratio? The intensity of a spectral line will increase to a limiting value as the slit width is increased. But the background increases at a more rapid rate. Accordingly, it is wise to use the finest slit width to obtain the highest line-to-background ratio. In reducing the slit width, however, a point is reached beyond which other gremlins enter the picture. In a grating instrument, for example, satellites may begin to appear at very narrow slits. In a prism instrument, the slit should be kept as fine as possible without introducing certain diffraction effects.

Earlier, we spoke of illumination in terms

of the resolution of the spectrograph. Equally important is illumination so adjusted that the spectral lines are transmitted but all extraneous light is removed. For example, light from the incandescent electrodes should not be permitted to register on the plate. The best way of accomplishing this is to use a system of illumination whereby the electrodes are focused on an aperture on the optical bench. A hole then becomes the apparent source, the images of the electrodes blocked out before the slit by the aperture jaws. Another way of doing this is to focus the light on an aperture at the grating or prism. This, however, allows unwanted light into the spectrograph, some of which may be scattered and terminate in unwanted background.

Source. With some notable exceptions, it has been found that the d.c. arc yields the best over-all concentrational sensitivity. This seems to be related to the temperature to which the element is raised in the source. For example, at relatively low flame temperatures, the sensitivity of sodium is poorer than it is at higher arc temperatures. Vallee,² however, recently reported on the sensitivity of sodium in a high temperature flame that was produced by burning cyanogen. In this source, the sensitivity of sodium was as high or higher than that in a conventional arc. Theoretically, an optimum temperature for achieving the greatest sensitivity for a particular element should be possible. This is a temperature just lower than that necessary to produce transitions other than those resulting in "persistent" lines. In other words, if all of the energy is expended by the production of a single spectral line, that line will be strong. If, on the other hand, more energy is provided, the element will produce lines in addition to the persistent lines and at their expense.

This may be at least a partial explanation of the "cathode layer" effect. Used extensively in Europe today, this source has been shown by Strock³ and others to be more sen-

sitive than the conventional d.c. arc more commonly used in this country. In the cathode layer technique, the sample is made electrically negative. In addition, a very small sample (about 15 mg) is used and the electrode is very narrow ($\frac{1}{8}$ ") with a crater drilled in it to a depth of perhaps $\frac{3}{8}$ ". The arc gap is usually about 10 mm. By contrast, the more common d.c. arc excitation uses a $\frac{1}{4}$ " diameter electrode drilled to a depth of $\frac{3}{16}$ ", the sample is made positive and the gap is but 2-3 mm. A photograph of the profile of the arc column of a cathode layer burning reveals that the lines of a good many of the elements are considerably stronger at the cooler cathode. They taper off towards the anode. In addition, the line-to-background ratio is stronger at the cathode. No full explanation of the phenomenon has been offered. But part of the explanation may be that the temperature near the cathode is close to the optimum required to produce only the persistent lines of many of the elements. At the higher temperatures near the anode, other lines are excited, reducing the energy emitted by the persistent lines.

Another source of high sensitivity is the carrier distillation technique devised by Scribner and Mullin.⁴ It is used for the determination of relatively volatile elements in the presence of refractory ones. A material such as gallium oxide is added to the powder to be analyzed. This sweeps the volatile elements up into the arc to such an extent that when used originally for the analysis of uranium, lines of uranium were practically non-existent while the impurity lines were prominent.

In still another way, differences in volatility may be taken advantage of to produce the best signal-to-noise ratios for groups of elements. This is through a moving-plate analysis. The sample is burned to completion but every few seconds the plate is racked. By spotting the best time interval for a particular element, further improve-

ment in the sensitivity of that element is achieved.

Under exceptional circumstances, the use of an atmosphere other than air around the source should be considered. Owen⁵ has described a simple container in which electrodes may be flooded with gases such as carbon dioxide or one of the inert gases. These are useful in reducing the cyanogen bands so that elements with principal lines within these bands are detected more readily. They also prevent the formation of oxides the molecular spectra of which are usually complex and contribute to the background.

Electrodes. There has been renewed interest in carbon (as opposed to graphite) electrodes for improving sensitivity. Two papers^{6, 7} by Morrison, Rupp and Klecak claim extraordinary sensitivity for the determination of trace elements in nickel and silicon carbide when the sample is arced in argon using carbon electrodes. Treating elements almost individually, these workers have shown other techniques to be rewarding, e.g., a fast spectrograph and plate coupled with very short burning times in boiler cap electrodes for volatile elements such as mercury, arsenic and zinc.

Buffers. A spectrographic buffer is a material which, when mixed with the sample, improves the reproducibility and/or the sensitivity of the analysis. A buffer which enhances sensitivity must, itself, have a high ionization potential and should be reducing rather than oxidizing. Graphite seems to be the best over-all choice. Many spectrographers use graphite but, in addition, mix in such materials as lithium carbonate or zinc oxide. These serve to provide an internal standard and, with many materials, provide "smoother" burns to improve precision.

Chemical Treatment. Two types of improvement are made in a sample to be analyzed through appropriate chemical treatment: the elements sought may be concentrated by separation techniques; elements



(Courtesy Spec Industries, Inc.)

FIG. 2. Stallwood jet mounted inside chamber for arcing samples in nitrogen-free atmospheres. Argon-oxygen mixtures are frequently used to enhance sensitivity by several orders of magnitude.

with low ionization potential may be removed.

The importance of concentrating an element is obvious when an unlimited sample is available. The spectrographic plate "sees" the total number of atoms of an element. The more that can be placed in an electrode, the better the sensitivity of that element. Of the wide variety of reagents available for separating out trace elements, the organic ones such as dithizone, 8-hydroxyquinoline have been found to be particularly useful. Mitchell⁸ described the use of a mixture of 8-hydroxyquinoline, tannic acid and thionalide which will recover microgram quantities of Co, Ni, Mo, Zn, Sn, Pb, V, Cr, Ag, Au, Ga, Fe and

Cu in the presence of excesses of an aluminum carrier.

As stated, such separations have a double purpose. They concentrate in a small volume the elements sought. They also remove the alkalis and other elements of low ionization potential. Such elements, by keeping the ionization potential at the arc low, prevent elements of higher potential from producing spectral lines.

Photographic Emulsion. When an unlimited sample is available, the plate chosen for the analysis need not be a high speed one. In fact, it is generally advisable to use a plate of moderate speed to take advantage of its other superior qualities. A moderate speed

plate usually has a fine grain, processes readily, has a low fog level and high contrast.

An emulsion with these characteristics is Spectrum Analysis #1. It has excellent resolution, excellent processing characteristics, a very low fog level and is sensitive over the region 2200–4300Å, where most of the lines of the elements appear. On the minus side, it has a variable contrast with wavelength changes and beyond 3600Å its contrast is so high that an element can be determined through only a single decade of concentration, e.g., from 0.01 to 0.1 %.

The photographic emulsion used will depend on which elements are sought. For example, if arsenic were sought in an organic ash, it would pay to use a fast emulsion such as 103-0. Because it is so volatile, arsenic requires but a short exposure. The alternative would be to superimpose a number of exposures on a slower emulsion such as SA #1.

In trace-element work, it is always desirable to run exposures until the sample is totally consumed. In this fashion, refractory elements will not escape detection. In doing this, however, chances are that many lines will be over-exposed. To accomplish both simultaneously, the use of a step-sector or step-filter is recommended. The exposure for one line will be optimum at one step; for another, at another step.

Sample Size Limited (Microanalysis)

Introduction. In the first part of this article, we spoke of the *double* problem of trace-element analysis. At one extreme, the sample could be unlimited in size—drinking water for example. At the opposite extreme, the sample could be exceedingly small—a particle of dust. The first part of the article dealt with the former. Here we discussed techniques for obtaining the optimum sensitivity with such samples. We showed how the important consideration was the line-to-background ratio. Anything we could do to

increase that ratio would improve sensitivity. Such techniques as using replicate exposures, concentration by ashing or chemical separation, the use of high-resolution, low-fog photographic emulsions, all resulted in increasing the line-to-background ratio and, consequently, improved sensitivity. Further, we showed that a fine entrance slit at the spectrograph should be used and the spectrograph itself should be set to its highest effective dispersion. Practically all the recommendations had the effect of improving the signal-to-noise ratio but at the expense of speed.

By way of contrast, *speed* is the key word when a micro sample is to be analyzed. For the analysis of a sample, the size of which is limited, necessitates getting adequate registration on a photographic plate. The sample is usually so small that nothing can be done to it chemically. Indeed, sometimes the sample is so small that even maneuvering it into an electrode is a feat in itself.

Typical examples of micro sample analysis in metallurgy are the examination of a microscopic inclusion in a casting and the identification of a surface deposit. In criminology, analyses of limited samples are everyday affairs. Some months ago we were shown a section of the skull of a murdered woman, on the surface of which was a shiny, grayish spot. Apparently, she had been struck with a metallic object. A pewter candlestick, found nearby, just about proved to be the murder weapon when the spectrum of scrapings from the skull matched that of the candlestick.

Biological research is another field where samples of limited size occur. Many biological projects end up with a speck of a newly isolated substance. Then comes the arduous task of analysis. Through spectrochemical analysis, vitamin B-12 was found to be a cobalt compound and carbonic anhydrase was confirmed as a zinc metallo-organic. Atomic energy research is still another field where tiny samples abound. In

recent years, a dozen or so new elements have been discovered. The birth announcement of almost every one of these elements was its unique emission spectrum.

The limited sample differs from the unlimited one in still another respect. In the former, we are concerned with *major* elements in a *tiny* sample; in the latter, with *trace* elements in a *large* sample. The matrix effect thus becomes important when dealing with a limited sample. Suppose a sample, the total weight of which is but a few micrograms, consists of 99 % sodium and 1 % iron. The iron would undoubtedly escape detection because of the low ionization potential of the sodium. If the spectrographer were asked to compare the iron content of this sample with one equally small which consisted of 99 % aluminum and the same 1 % iron, he might be thrown completely off the track by the appearance of the two spectrograms. For, in the latter, iron lines undoubtedly would appear.

The conclusion from the above is that quantitative, even semiquantitative, reports on limited samples are usually not possible. With fingers crossed, we report "major" or "principal" or "minor" elements. But on unlimited samples, semiquantitative reports are indeed possible. We can ash organic samples or evaporate down several water samples, mix the resulting powders with graphite in a fixed ratio and then analyze the samples by referring to standards such as the Spex Z or G sets. Here we can report values such as .003 % or .00005 % and obtain excellent comparisons among the samples.

The Excitation Source. So much for the differences in the two problems. We have already stated that to analyze limited samples, we must obtain the maximum speed from our apparatus. Let us examine every step in the spectrochemical procedure to see how we can obtain the highest speed from each.

The d.c. arc with the sample burned to completion has been found to be the best over-all source. The sample is ordinarily

made electrically positive for the anode is the hotter of two graphite electrodes. Certain elements, however, have more intense lines near the cathode and it is often desirable to take advantage of this fact. The spectrograph is allowed to "see" only the light emitted from a thin layer directly above the cathode.⁸ To utilize the "cathode layer" phenomenon, it is advisable to use a stigmatic spectrograph.

A source approaching, and in certain instances surpassing, the sensitivity of the d.c. arc is the copper spark. With this technique,⁹ a drop of the solution to be analyzed is placed atop the faced-off ends of two $\frac{1}{4}$ " copper rods. After drying, the rods are sparked for 5 to 10 seconds. Because the source requires solutions, it is not so universally applicable as the d.c. arc. Where applicable, excellent results have been obtained. For example, as little as 20 millimicrograms of Ag, Al, Bi, Cu, Fe, Mg, Mn, Pb, Sn and Tl can be detected.

Other sources occasionally used are enclosed ones like the hollow cathode tube. The principal advantage here is that the sample may be excited over and over again. In contrast, an atom once excited in an open source disappears.

Spectrograph. To obtain the best speed on any spectrograph, all possible light from the source should be focused on the slit. In addition to using condensing lenses, sometimes large reflectors are placed behind the source in order to collect as much of the light as possible and direct it to the spectrograph.

As was pointed out earlier, it is a good idea to mask out the incandescent electrodes so that their light does not result in unwanted background. In the past, too little attention has been paid to this. But many spectrographers have recently augmented the train on their optical bench with an adjustable mask and an additional condensing lens in order to mask out the electrodes.^{8, 10}

On the subject of external optics, fused silica should be mentioned. Synthetically prepared, this material has about the same

transmittance as natural quartz down to about 2300A where the latter starts to fall off considerably. Some grades of fused silica transmit a usable amount of the incoming radiation down to 1650A. For the determination of cadmium, lead, zinc, carbon, phosphorus, sulfur, selenium, etc., fused silica offers decided advantages.

With speed again in mind, a small spectrograph is preferred over a larger one. The f-number of spectrographs generally varies directly with their size so that the larger the spectrograph, the slower it is. The grating instrument should be set to the region of greatest speed. The blaze of a grating will determine its speed so that a particular grating will be many times as fast in one order than in another. If in the 3rd order, a particular spectrograph is five times as fast at 2881A than at any other order, the spectrograph should be set for the 3rd order for the determination of silicon in a limited sample. The slit should be set as wide as possible, consistent with the resolution required for the analysis.

One scheme to increase the speed of a spectrograph was recently tried successfully. A university needed the greatest possible speed in a spectrograph over a wavelength interval of about 100A. At the same time, a dispersion of 2.5 A/mm was specified. As has been mentioned, such high speed and high dispersion do not ordinarily go together. To increase the speed, a cylindrical lens (axis horizontal) was used right at the camera, condensing the light vertically as it emerged from the grating of the instrument. In other words, light on a 10-mm high slit wound up as spectral lines but 1 mm high, giving a theoretical 10-fold increase in illumination at the camera. While the scheme had the disadvantage of possessing a limited wavelength coverage, it was sw hon to give this 10-fold increase in apparent speed for the wavelength interval in question. Moreover, any 100A interval could be chosen by setting the instrument so that the desired range was behind the lens.

Photographic Emulsion. With speed again the goal, a high-sensitivity photographic emulsion is required. An ideal emulsion would be extremely fast over several thousand angstroms and still retain good resolution and other characteristics. Unfortunately, compromises have to be accepted. There are a number of emulsions having high speed over comparatively narrow wavelength bands. Examples are given below:

Emulsion	Approx. W. L. Range, A
Ilford Q-2	60-2000
Eastman 103-0	2300-5000
Eastman I-N	6500-8200

Eastman also sensitizes certain emulsions for the region 2100-2500A through the use of fluorescent dyes. The speed of 103-0 in this region may be so increased. This emulsion, so treated, is called 103-0 (U.V.).

One scheme that is sometimes used to increase the sensitivity of an emulsion is to "prefog" it. The characteristic curve (density vs. exposure) consists of a "toe" region at low density values followed by a straight line as the exposure level increases. Deliberately fogging a plate takes the emulsion out of its region of low sensitivity. This scheme, however, is seldom used because of the inconvenience in fogging a plate reproducibly.

Practically speaking, many experienced spectrographers use the 103-0 emulsion as a general-purpose tool when running tiny samples. It has a wide wavelength coverage and its speed, determined in a recent series of tests by A.S.T.M., ranges from 5 to 40 times that of Spectrum Analysis #1, depending on the wavelength.

Conclusions. This subject of trace-element analysis should rightly be considered just begun rather than concluded. Metallurgists, biologists, chemists and physicists are rapidly learning that many of the properties which they assigned to materials are grossly inaccurate because the materials themselves are not pure. Perhaps the most spectac-

ular example of this is the transistor properties of silicon. One of the more common elements, silicon had been studied and its electrical properties supposedly known for decades. But when *pure* silicon was prepared, within the past few years, it was found to have decidedly different properties, so wonderfully different that silicon transistors, rectifiers, and other semiconductor devices are making serious inroads on older counterparts.

The role of the spectrograph will become increasingly important as pure materials find their place in technology. The problems will become increasingly taxing as demands are made to maintain the quality of these pure materials.

REFERENCES

1. HARRISON, G. R., LORD, R. C., AND LOOFBOUROW, J. R., "Practical Spectroscopy," Prentice-Hall, 1948.
2. VALLEE, B. L., unpublished paper at Trace Element Symposium held in New York, November, 1955.
3. STROCK, L. W., "Spectrum Analysis with the Carbon Arc Cathode Layer," Hilger, London, 1936.
4. SCRIBNER, B. F., AND MULLIN, H. R., *J. Res. NBS*, **37**, 369 (1946).
5. OWEN, L. E., *J. Opt. Soc. Am.*, **41**, 139 (1951).
6. RUPP, R. L., KLECAC, G. L., AND MORRISON, G. H., *Anal. Chem.* **32**, 931 (1960).
7. *Ibid.*, p. 933.
8. MITCHELL, R. L., "The Spectrographic Analysis of Soils, Plants and Related Materials," Commonwealth Bureau of Soil Science, Harpenden, England, 1948.
9. FRED, MARK, NACHTRIEB, N. H., AND TOMKINS, F. S., *J. Opt. Soc. Am.*, **37**, 279 (1947).
10. TWYMAN, F., AND SIMEON, F., *Trans. Opt. Soc.*, **31**, 169 (1929-30).

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TUNGSTEN ANALYSIS*

The emission spectrograph offers an excellent means of controlling trace impurities in tungsten throughout the stages of manu-

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facturing from the ore to the finished product. Processing the ore involves a combination of hydro- and powder metallurgy.⁸ The control of critical impurities is very important in the chemical processing steps from ore digestion to the final gray metal powder. Tungstic oxide is prepared quite pure, after which, certain elements are often added in trace amounts in various processing steps to control the properties of the resulting metal powder or finished product. Additives such as silica and alumina act as cleansing agents during the sintering of the ingots and also as grain growth inhibitors. On the other hand, iron as a residual impurity must be kept low, since its presence lowers the recrystallization temperature in tungsten wire.

The emission spectrum of tungsten is complex; several thousand lines fall in the range between 2000-10,000Å.⁷ In order to perform a satisfactory analysis, either a large spectrograph with good dispersion is needed or a method of eliminating or depressing the tungsten spectrum. Very little has been published up to the present time on determining trace elements in tungsten. Only half a dozen scientific papers were found in the literature.^{3, 5, 6, 9, 10, 12}

Tungsten and its compounds will give a suitable spectrum when excited in a d.c. arc, a.c. arc, and a.c. spark; however, the sensitivities for trace elements vary widely. Graphite electrodes are generally the most satisfactory means for holding the samples during excitation. Tungsten spectra generally have considerable background radiation present, but this can be controlled with a buffer or suitable optics and diaphragms before the slit of the spectrograph.

Variations of the above basic excitation sources have been developed which include the ignited a.c. arc, uni-arc, and sustaining a.c. arc. Recent publications describe the use of these sources on refractory metals such as zirconium, titanium, etc., to obtain good sensitivity when arcing metal pieces by the

point-to-plane technique.⁴ The author has not used these sources and techniques on tungsten, but feels they would be applicable. Some of the difficulties encountered when arcing these refractory metals by the point-to-plane technique are the preparation of standards and erratic results caused by segregation.

The three basic excitation sources will be discussed below in relation to sensitivities attainable with various types of sample preparation. Special emphasis will be given to the use of the high voltage Duffendack type a.c. arc for obtaining maximum sensitivities in trace element detection.²

The d.c. arc is good for general qualitative work on powder samples and gives adequate sensitivity for most problems. Generally, there is considerable background present in the spectrum when a sample is arced directly; the addition of graphite powder will reduce this somewhat. The d.c. arc gives the best sensitivity when the tungsten is arced as the metal powder. The addition of graphite to the tungsten powder lowers background only to a slight extent at low amperages. At high amperage d.c. excitation, above 10 amperes, there is a marked depression of background and tungsten spectrum; but the tungsten carbide formation is not as pronounced as with the high voltage a.c. arc to give maximum sensitivity.

Arcing samples in the form of ammonium paratungstate, tungstic acid, and WO_3 result in a loss of sensitivity, especially on medium volatility and refractory elements, by more than a magnitude. The sensitivity for volatile elements such as arsenic and lead is not greatly affected. Arcing powdered sodium tungstate gives fair sensitivity for most trace impurities, but for best results the material should be anhydrous. The excitation of solid tungsten samples in the form of rods, wire, or disks, when used as self-electrodes, does not give the sensitivity attainable with powders.

The a.c. spark can be used to excite solid samples of tungsten, but again the sensitivity

for trace elements present is poor. However, the use of the powder spark method of pelleting samples of sodium tungstate or tungstic oxide with National graphite SP-1 powder gives a good spectrum with fair sensitivity and excellent precision.¹² The use of secondary tungsten lines for internal standardization will not work well unless the erratic formation of tungsten carbide is controlled during sparking. For example, in matrices other than sodium tungstate, the addition of pure anhydrous sodium tungstate to the tungstic oxide pellets will depress this effect. Powders in these two forms seem to make the best pellets for spark analysis. By spark excitation, molybdenum could be determined at the 0.001 % level using the 3132.594 Å line.

The high voltage Duffendack a.c. arc operating at 2200 volts was found to give maximum sensitivity for trace elements when the tungsten is excited as the metal powder in the presence of graphite. No regular commercial source units are available which give more than 5 amperes. Greater amperage is needed to obtain maximum sensitivity. The advantage of this source in analyzing tungsten as the metal powder is that when a buffer of graphite is added, a highly refractory matrix of tungsten carbide is formed in the arc.³ This formation holds back the tungsten spectrum as in carrier distillation techniques and volatilizes out the impurities. This effect is not noticeable at low amperages. It begins at about 4–5 amperes and 7–10 amperes are needed to get adequate carbide formation. X-ray diffraction studies confirmed this phenomenon.

The tungsten spectrum is held back for up to 2 minutes. A very hot arc is formed and a large increase in sensitivity results for medium volatility and refractory elements. The limit of detection for volatile elements like arsenic and lead are only slightly improved. The addition of nickel or cobalt as an internal standard element to the graphite buffer gives excellent results. A ratio of six parts of tungsten powder to one part graphite buffer

EMISSION SPECTROSCOPY—LIGHT

TABLE 1

Element and Line Å	Matrix	Limits of Detection ^a		
		D.C. arc Direct Load	A.C. Spark Pelletted With Graphite	A.C. Arc With Graphite
Al 3092.713	W	10 ⁻⁶	10 ⁻⁵	10 ⁻⁷
	WO ₃	10 ⁻⁵		
	Na ₂ WO ₄	10 ⁻⁶		
As 2860.452	W	10 ⁻⁵		10 ⁻⁵
	WO ₃ ^b	10 ⁻⁴		
Ca 3933.666	W	10 ⁻⁶		10 ⁻⁶
	WO ₃	10 ⁻⁵		
	Na ₂ WO ₄	10 ⁻⁶		
Cu 3273.962	W	10 ⁻⁷		10 ⁻⁷
	WO ₃	10 ⁻⁶		
Fe 2483.027	W	10 ⁻⁶	10 ⁻⁶	10 ⁻⁷
	WO ₃	10 ⁻⁵		
	Na ₂ WO ₄	10 ⁻⁶		
K 7664.907	W	10 ⁻⁵		10 ⁻⁵
	WO ₃	10 ⁻⁵		
Mg 2795.53	W	10 ⁻⁷		10 ⁻⁸
	WO ₃	10 ⁻⁶		
	Na ₂ WO ₄	10 ⁻⁷		
Mo 3132.594	W	10 ⁻⁶	10 ⁻⁵	10 ⁻⁴
	WO ₃	10 ⁻⁵		
	Na ₂ WO ₄	10 ⁻⁶		
Na 5889.953	W	10 ⁻⁶		10 ⁻⁶
	WO ₃	10 ⁻⁶		
Ni 3414.765	W	10 ⁻⁶	10 ⁻⁵	10 ⁻⁷
	WO ₃	10 ⁻⁵		
Si 2506.899	W	10 ⁻⁶	10 ⁻⁴	10 ⁻⁷
	WO ₃	10 ⁻⁵		
	Na ₂ WO ₄	10 ⁻⁶		
Th 2899.724	W	10 ⁻⁴	10 ⁻³	
	WO ₃	10 ⁻⁴		

^a Sensitivity is expressed as grams of element per gram of sample; e.g. 10⁻⁵ = 1-10 ppm = 0.0001-0.001%.

^b Using a d.c. arc with boiler cap electrodes, WO₃ was arced with graphite and ZnO on a Bausch & Lomb dual grating spectrograph. A sensitivity of 1 ppm was reached using the 2288.12 Å, As line.

works well. High purity nickel or cobalt sponge ground to pass 200 mesh is added to graphite at the 1% level.

For other than the volatile elements, tungsten in the form of ammonium paratungstate, tungstic acid, and tungstic oxide can be converted to the metal powder by careful reduction. Even wires, pieces of rod and disks can be oxidized to tungstic oxide and then reduced to the metal powder for analysis. Temperatures of 650-700°C are needed for the oxidation and 800-900°C for hydrogen reduction.

In Table 1, approximate sensitivities are given for some of the common elements determined in tungsten by direct means without preconcentration. Unless otherwise stated, a large Littrow Bausch & Lomb quartz spectrograph was used. The sources were as follows: 250 volt d.c. arc, 5-20 amperes; National Spectrographic Laboratories, Inc. a.c. spark source, model J4200; and a Duffendack high voltage a.c. arc, 2200 volts, 2.5-15 amperes. National and United high purity graphite electrodes were used. For powders, 1/4 inch diameter electrodes were beveled and a crater 1/8 inch in diameter and 1/8 inch in depth, with a wall thickness of .010 ± .002 inch, were used. Electrodes were filled with sample by tamping. The powder pellets used in the spark work were prepared on an Applied Research Laboratories' briquetting press. They were made to just fit in a 1/4 inch diameter electrode with a crater of 0.194 inch in diameter and 1/8 inch in depth. The counter electrode has a 15° cone shaped tip made from 1/4 inch graphite stock. The spectrographic plates used were EK33 and 1 L.

When other refractory metals, which form the carbide easily, are present as impurities in tungsten, their limits of detection will be greatly reduced when using the a.c. arc technique. These elements will be depressed along with the tungsten. For example, the detection of molybdenum will be reduced approximately from 0.0005% to about 0.05%.

The determination of tungsten itself as a trace element does not lend itself to low levels of detection unless some chemical enrichment technique is used.¹ Generally, the addition of graphite powder to the sample should be avoided since sensitivity will be depressed because of the formation of tungsten carbide in the arc. By buffering a molybdenum metal powder sample with zinc oxide, a sensitivity of 0.005 % tungsten was attained using the 4008.753 Å line. A Bausch & Lomb dual grating spectrograph was used with d.c. arc excitation.

REFERENCES

1. AHRENS, L. H., "Spectrochemical Analysis", Addison-Wesley Press, Reading, Mass., pp. 200-01, 1950.
2. DUFFENDACK, O. S., WOLFE, R. A., *Ind. Eng. Chem., (Anal. Ed.)*, **10**, 161 (1938).
3. DYCK, R., VELEKER, T. J., *Anal. Chem.*, **31**, 390-92 (1959).
4. FARRELL, F. F., HARTER, G. J., JACOBS, R. M., *Anal. Chem.*, **31**, 1550-54 (1959).
5. GENTRY, C. H. R., MITCHELL, G. P., *Metalurgia*, **46**, 47-51 (1952).
6. LOUNAMAA, NÜLO, *Spectrochim. Acta*, **4**, 400-12 (1951).
7. "M.I.T. Wavelength Tables," (Harrison, G. R., ed), Wiley, New York, 1939.
8. NELSON, R. C., *Mines Mag.*, **47**, 68-73 (1957).
9. PARSONS, S., *J. Opt. Soc. Am.*, **33**, 659 (1943).
10. PHELIN, J. M., Congr. groupe. avance. method. anal. spectrogr. prod. met. 7th Congr. 1947, 51-6, Paris.
11. SMITHELLS, C. J., "Tungsten", 3rd ed., Chapman & Hall, London, 1952.
12. VELEKER, T. J., DYCK, R., *Anal. Chem.*, **31**, 387-90 (1959).

THOMAS J. VELEKER

VACUUM ULTRAVIOLET. SEE VACUUM SPECTROSCOPY.

VISUAL SPECTROMETERS, MONOCHROMATORS, ILLUMINATORS

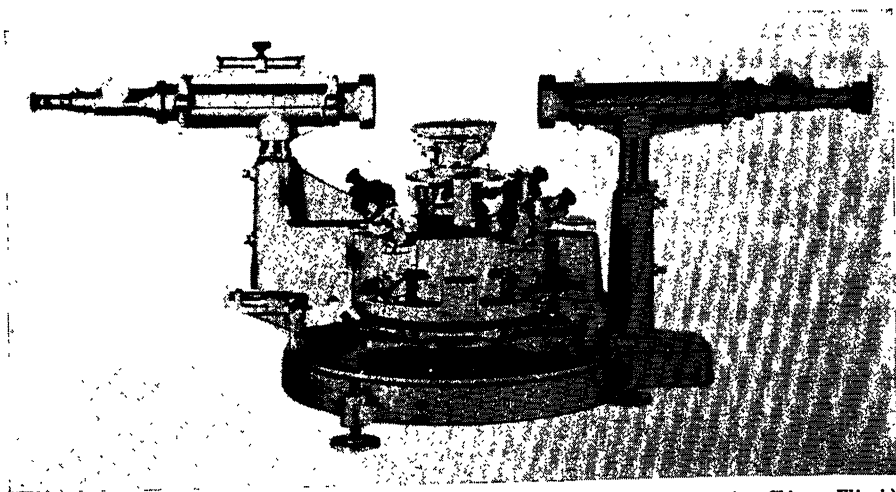
It is difficult to distinguish between the terms "spectrometer," "monochromator" and "illuminator," because frequently the same instrument can be designated by all three. Strictly speaking, however, an instru-

ment can be called a spectrometer if it can be employed for measuring the wavelengths of a series of lines; a monochromator if it can isolate a spectrum line, not necessarily measuring the wavelength; and an illuminator if it isolates the line and serves to illuminate a specimen or additional optical equipment, such as a microscope. While it may be possible to employ the same apparatus for all three functions, the spectrometer should lay greater stress on precision of setting and less on aperture ratio, the monochromator may emphasize spectral purity, and the illuminator normally sacrifices spectral purity and precision of measurement for a high aperture ratio and high light output.

The substitution of photoelectric and other radiation detectors for the human eye has confused such historical differences, however, so that for lack of a better name the dispersing elements of scanning spectrophotometers are referred to as spectrometers or monochromators. A "spectrometer" displays the spectrum for the multiple exit slits of direct reading emission equipment.

In the following description, instruments are called spectrometers although in the same form they are frequently used as monochromators or illuminators.

Prism Spectrometers. Much of the early work in spectroscopy was performed on a simple, divided circle prism spectrometer (Fig. 1). The slit-collimator arm is usually fixed, while the telescope arm rotates about a vertical axis at the center of the prism tables. Its angular position can be read from the fixed divided circle and a vernier on the telescope. Usually the smaller prism table can also be rotated about the same axis. The lenses should be achromatic or the telescope provided with a focusing adjustment (Gaertner, Hilger & Watts). If the constants of the Hartmann or Cauchy formulas for the refractive index of a prism material are known, the wavelengths of unknown lines can be computed from their observed angles, or conversely, if wavelengths are known, the refractive indices of the prism material can



(Courtesy Gaertner Scientific Corporation, Chicago, Illinois)

FIG. 1. Gaertner precision spectrometer, with circle graduated in 5-minute divisions, reading by vernier to 1 second, used particularly for measuring the optical constants of glasses and other optical materials.

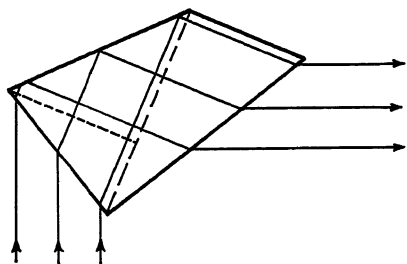


FIG. 2. Pellin-Broca prism for producing a spectrum always at 90° to the incident beam.

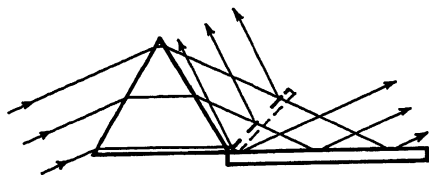


FIG. 3. Wadsworth prism mounting, to produce a spectrum in a direction always parallel to the incident beam, or, by tilting the mirror, always perpendicular.

be determined. Nowadays divided circle spectrometers are employed for instructional purposes. In a highly accurate form, with divided circles reading to .1 second of arc (Gaertner, Hilger & Watts, Galileo, Jobin & Yvon), they are employed as fundamental

tools for measuring the refractive indices of optical glasses or crystals of all types, for several different wavelengths, to determine the dispersion or constants of the Hartmann or Cauchy formulas.

Usually an observer prefers to remain seated in one position with a light source also fixed, and observe various regions of the spectrum merely by turning a knob. This can be achieved by a constant deviation spectrometer, which employs either a Pellin-Broca prism¹ (Fig. 2), or by a mounting suggested by Wadsworth (Fig. 3).² The prism can be driven by a screw, with a drum or spiral calibrated to read wavelengths directly.

The Pellin-Broca mounting with simple lenses is employed in the visible range, where slight refocusing is tolerable (Gaertner, Bausch & Lomb, Hilger & Watts, Zeiss). In the ultraviolet or in the infrared, particularly with crystal quartz, where a Cornu prism must be employed, the Wadsworth arrangement is used, with mirrors instead of lenses, to avoid refocusing (Gaertner, Hilger & Watts). Several manufacturers supply camera attachments which convert such spectrometers into simple spectrographs.

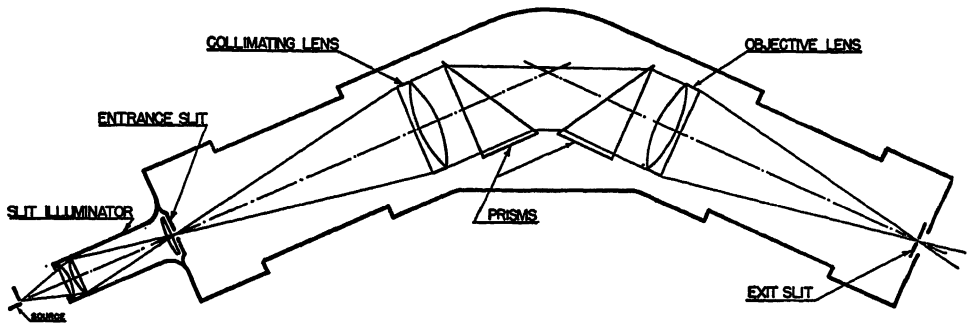
The fixed deviation makes it possible to gang two such spectrometers together to form a double monochromator, for high spectral purity and low scattered light (Hilger & Watts).

A Young-Thollon arrangement of two 30° quartz or glass prisms rotating symmetrically about axes, as indicated in Fig. 4, and quartz-lithium fluoride achromatic lenses has been employed by Farrand Optical for an ultraviolet monochromator.

In the Hilger-Mueller design of double monochromator (Fig. 5), lens surfaces are worked on the face of the dispersing prisms in order to reduce the number of surfaces and thus increase the over-all transmission

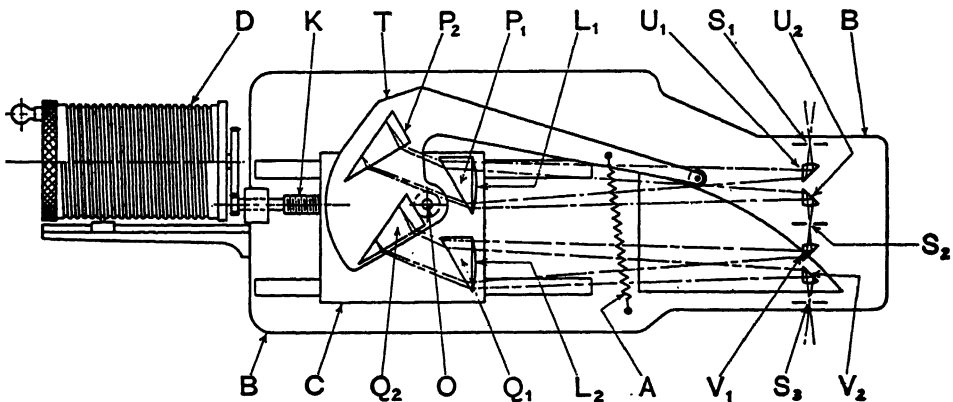
of the instrument. The single screw drive automatically adjusts focus and tilts the prisms to produce the wavelength indicated by the drum. Because of the difficulty of producing the lens surfaces on the prisms, and for greater mechanical simplicity, Hilger & Watts has now replaced this design by a double Littrow mirror system.

In ultraviolet spectrophotometers, Beckman, Hilger & Watts, Unicam, Jobin & Yvon and Shimadzu have employed a simple Littrow prism system with a concave mirror focusing element (Fig. 6). The prism needs only to be rotated to change the wavelength range, and a wavelength scale can be calibrated to read directly in millimicrons.



(Courtesy Farrand Optical Company, New York)

FIG. 4. Young-Thollon monochromator. To change wavelengths, the prisms are rotated symmetrically about the axes.



(Courtesy Hilger & Watts, Ltd., London, England)

FIG. 5. Hilger-Mueller double monochromator. To save reflections, lens surfaces are worked on the faces of the prism.

EMISSION SPECTROSCOPY—LIGHT

Perkin-Elmer, Baird-Atomic, Hilger & Watts and Unicam in their infrared spectrophotometers employ a similar Littrow prism system, usually of higher flux transmitting power, obtained from a 60° prism and back mirror rather than a 30° prism with reflecting back face. Figure 7 shows a typical arrangement.

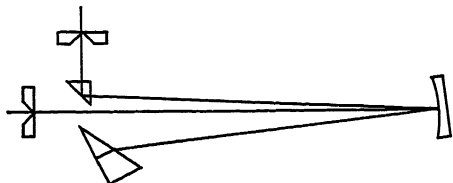
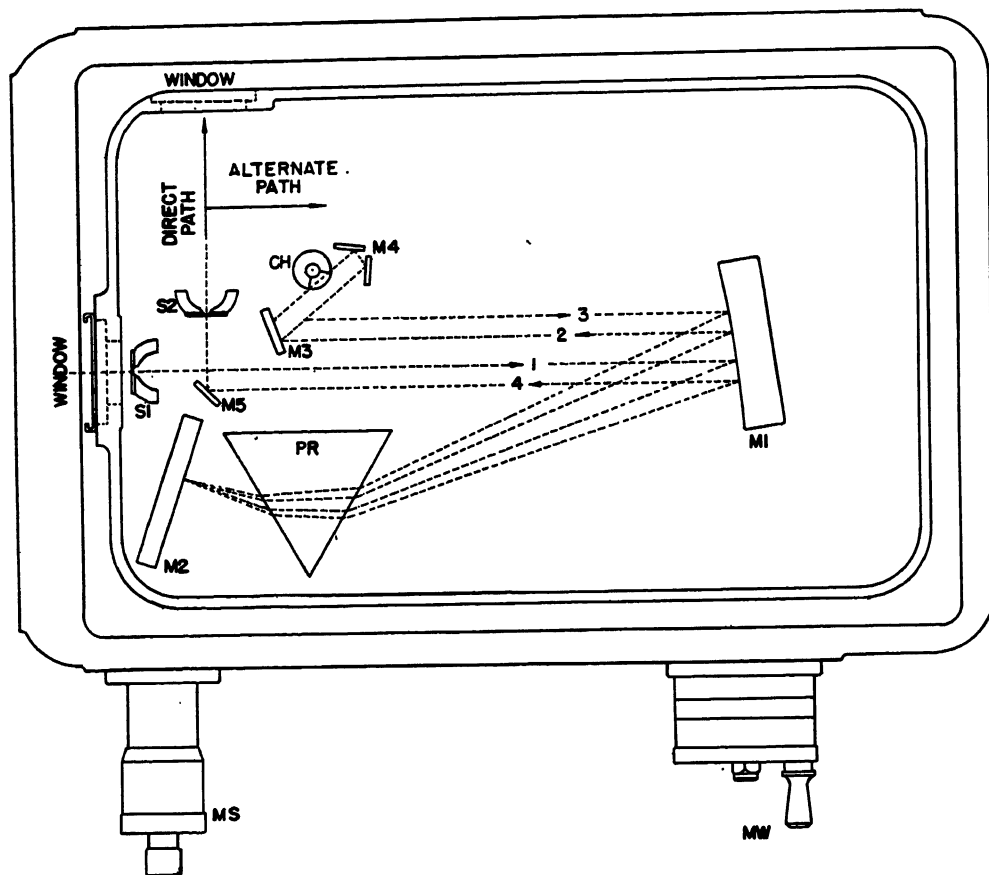


FIG. 6. A typical Littrow prism monochromator as used in ultraviolet spectrophotometers.

range. If, after passing once through the optical system, the light is intercepted before the exit slit and returned once more through the system, chopped at some frequency to which the amplifier is tuned, the scattered light may be reduced as in a double monochromator.³ Such a spectrometer is said to be "double passed."

For maximum spectral purity in spectrophotometry it is best to employ a double monochromator. The Applied Physics (Cary) designs illustrate two typical optical systems: Fig. 8 shows a two prism combination and Fig. 9 a prism-grating arrangement.

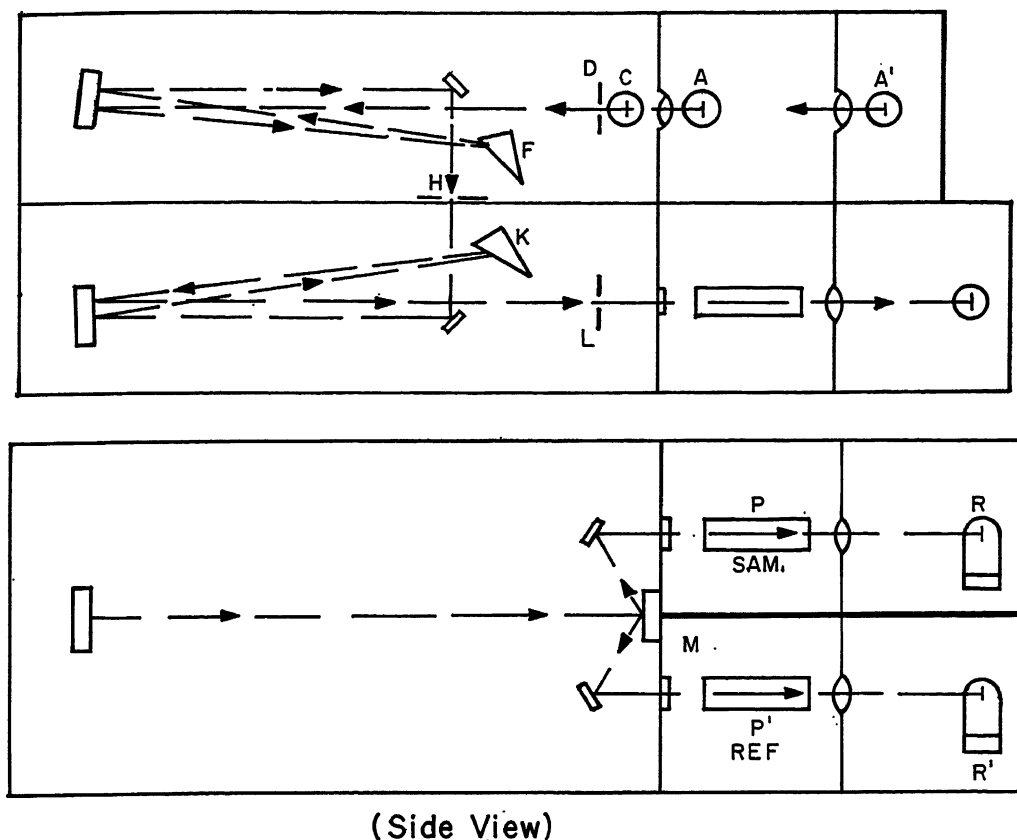
Unicam, in their simple spectrophotometer, employ a Féry prism mount, similar to



(Courtesy Perkin-Elmer Corp., Norwalk, Conn.)

FIG. 7. An infrared prism monochromator, double passed to reduce scattered light.

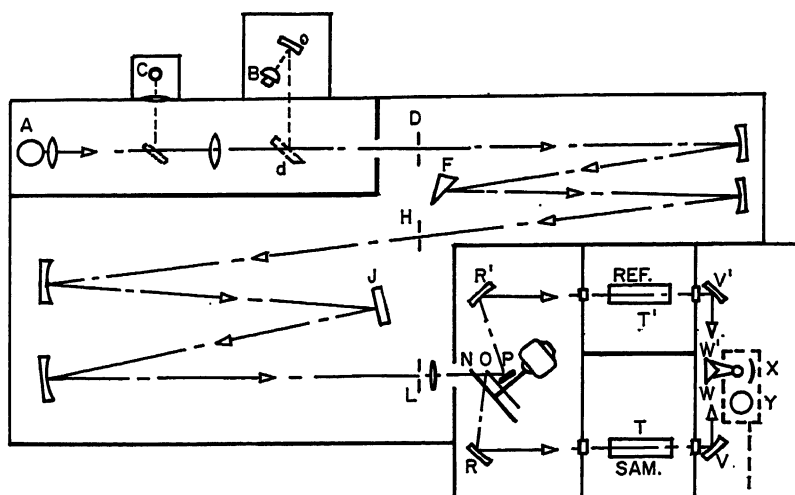
VISUAL SPECTROMETERS, MONOCHROMATORS, ILLUMINATORS



(Side View)

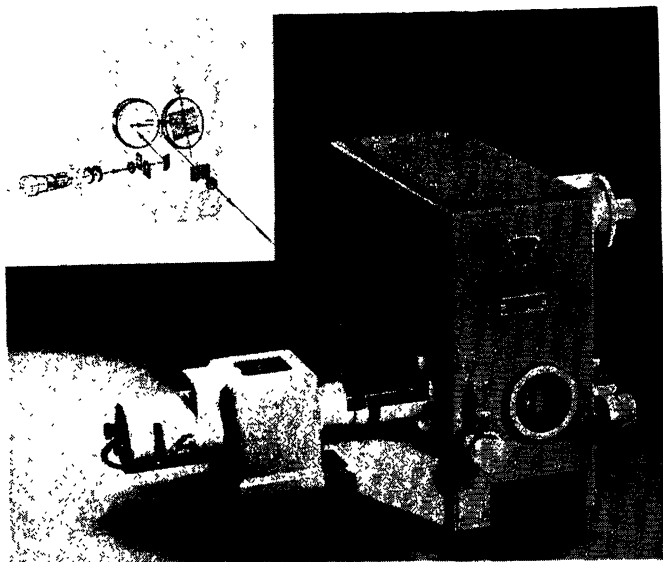
(Courtesy Applied Physics Corp., Pasadena, Calif.)

FIG. 8. A two prism, mirror-double monochromator.



(Courtesy Applied Physics Corp., Pasadena, Calif.)

FIG. 9. A prism grating double monochromator.



(Courtesy Bausch & Lomb Optical Co., Rochester, N. Y.)

Fig. 10. A high aperture grating illuminator.

the Féry spectrograph arrangement. (See pages 269–270.)

Grating Spectrometers. For many years original gratings have been too expensive and too scarce to be employed commercially in spectrometers or monochromators. Such replica gratings as were available had too high a level of scattered light and too poor definition to compare with prisms in performance. However, since 1952, with the development of replication techniques capable of producing replicas comparable in performance to an original ruling and equivalent in price to a prism, plane replica gratings have been increasingly employed in spectrometers, in the following designs.

Bausch & Lomb have developed a mounting (Fig. 10) which is designed primarily as an illuminator because its relatively high aperture ratio, approximately $f/4$, is achieved at a loss in definition as a result of aberrations. The wavelength dial reads directly in millimicrons.

Fastie,⁴ for Leeds & Northrup, re-discovered a grating spectrometer system originally described by Ebert⁵ in 1889 (Fig. 11). Fastie

pointed out that if the slits were arcs of a circle centered about the extended axis of the concave mirror, high resolution could be maintained even when using long entrance and exit slits. Fastie also applied a sine bar drive to the rotation of the grating to produce

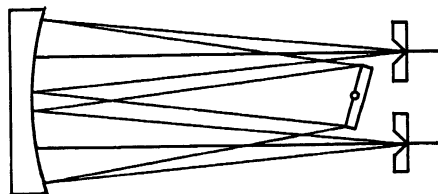


Fig. 11. Fastie-Ebert grating spectrometer. A "sine bar" rotation of the grating produces a drive linear in wavelengths.

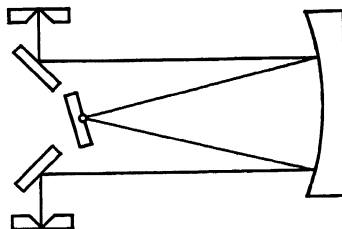


Fig. 12. Modified Ebert grating spectrometer.

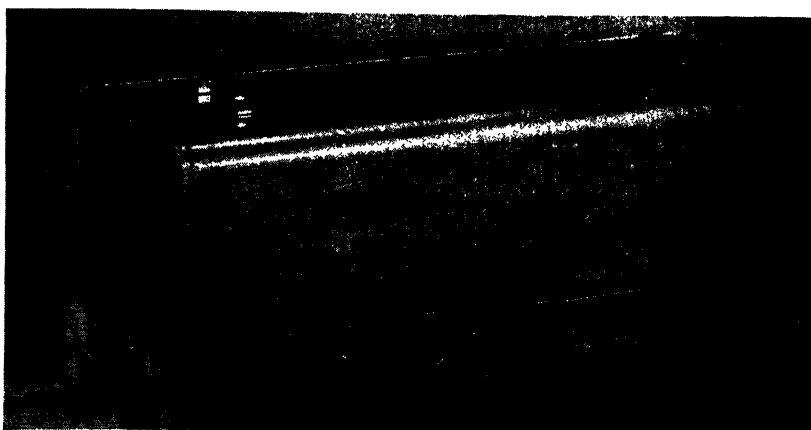


FIG. 13. .5 Meter Fastie-Ebert scanning grating spectrometer, giving .1 Å resolution.

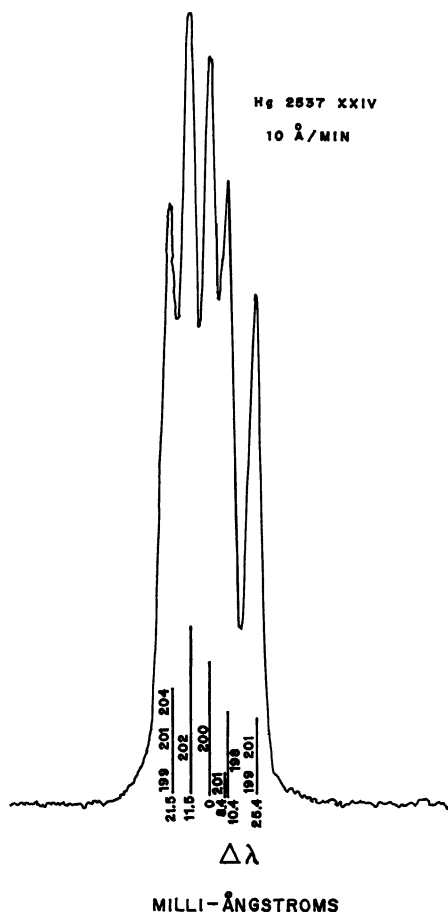


FIG. 14. Direct photoelectric scan of the Hg 2537 isotope hyperfine structure, using a Fastie-Ebert spectrometer, in the XXIV order of a grating of 7448 grooves/inch, showing resolution of .01 Å.

a direct wavelength read-out. The Leeds & Northrup spectrometer employed a 750-mm focal length and a grating of 30,000 grooves per inch and was claimed to yield a second order resolution of .05 Å. It has since been discontinued.

Modifications of the basic Ebert arrangement are employed by Farrand and by Hilger & Watts for inexpensive monochromators (Fig. 12).

Jarrell-Ash has produced a simple 500 mm Fastie-Ebert spectrometer (Fig. 13) with straight or curved slits, yielding second order resolution up to .1 Å at $f/8.6$, and one meter and 6 foot vacuum spectrometers for high resolution and precise wavelength measurements. The 6 foot model with appropriate photomultiplier and strip chart recorder will produce a direct intensity trace of the Hg 2536 Å line, with components separated by only .01 Å (Fig. 14). Wavelengths may be read directly to 1 Å and interpolated between standards to $\pm .02$ Å.

REFERENCES

1. PELLIN, P. AND BROCA, A., *Jour. de Physique*, **8**, 314 (1899).
2. WADSWORTH, F. L. O., *Astrophys. J.*, **1**, 232 (1895).
3. WALSH, A., *Nature*, **167**, 810 (1951).
4. FASTIE, W. G., *J. Opt. Soc. Am.*, **42**, 9, 641 (1952).
5. EBERT, H., *Wied. Ann.* **38**, 489 (1889).

R. F. JARRELL

EMISSION SPECTROSCOPY—LIGHT

VISUAL SPECTROSCOPES

The terms "spectroscopy" and "spectroscopic" are generic and are applied to the whole field of study which concerns itself with isolating a single wavelength or separating an array of electromagnetic wavelengths into a spectrum. Indeed, these terms are now applied to sound waves or electrical frequencies. It is most useful, however, to reserve the term "spectroscope" for a visual instrument for observing spectra, without taking a photograph (spectrograph) or making a precise wavelength measurement (spectrometer). A spectroscope usually has an arrangement for viewing either a comparison spectrum or a coarse wavelength scale.

The simplest of all spectroscopic instruments is a spectroscope consisting only of a slit which is viewed through a transmission grating. The observer sees a virtual image of the slit in the various colors of the spectrum (Fig. 1, Beck). A similarly compact prism spectroscopy is obtained by using an Amici¹ prism, consisting of two prisms of crown glass and one of dense flint glass (Fig. 2, Beck, Bausch & Lomb, Zeiss). Other direct vision prisms are the Zenger² and Wernicke³ (Figs. 3 and 4). A more refined transmission grating spectroscope may have a slit, collimating lens, grating, objective lens and eyepiece (Fig. 5). The original spectroscopy

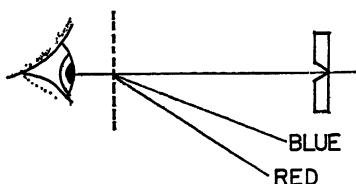


FIG. 1. Simple spectroscopy forming virtual images of a slit through a transmission grating.

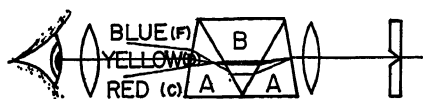


FIG. 2. Direct vision spectroscopy using an Amici prism, prisms A of crown glass, prism B of dense flint.

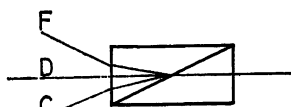


FIG. 3. Zenger prism.

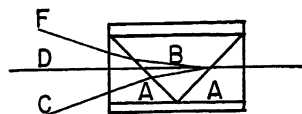


FIG. 4. Wernicke prism.

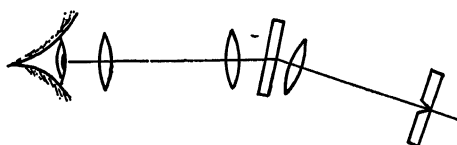


FIG. 5. Transmission grating spectroscopy.

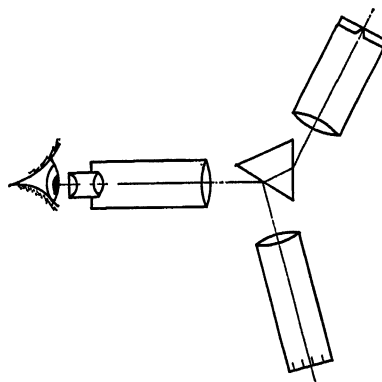


FIG. 6. Kirchhoff-Bunsen spectroscopy, with wavelength scale reflected from the third tube.

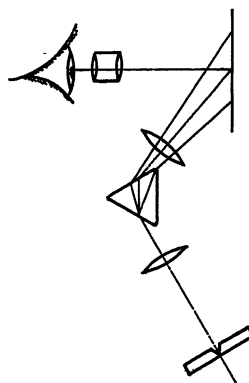
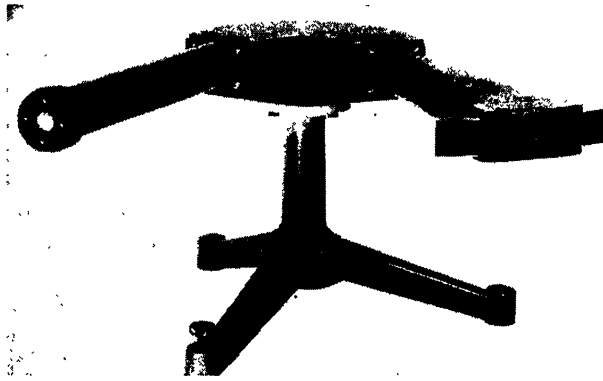


FIG. 7. Spectroscopy for the ultraviolet, with eyepiece viewing a fluorescent screen.



(Courtesy Hilger & Watts, London, England)

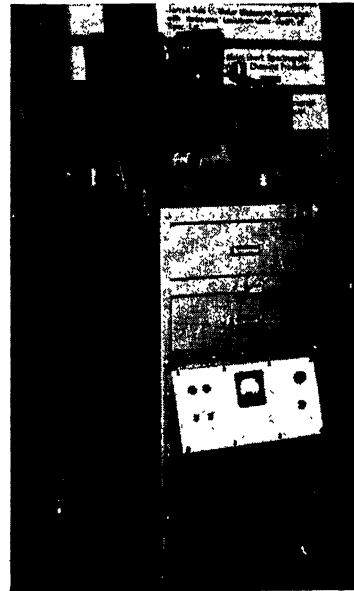
FIG. 8. The Hilger Steeloscope—a high dispersion spectroscope for rapidly grading or sorting steels visually.

used by Bunsen and Kirchhoff, 1860, employed a prism in a mounting with a third arm containing an illuminated wavelength scale, observed through the eyepiece by reflection off the prism face (Fig. 6, Gaertner). The telescope may be rotated through a small angle to observe different regions of the spectrum. Lenses must be achromatic or the telescope has to have a focusing adjustment. The ultraviolet region of the spectrum can be observed visually by projecting the spectrum on a high efficiency fluorescent screen which is viewed by the eyepiece (Fig. 7, Beck).

Simple visual spectroscopes are employed to study qualitatively the emission of flames or other sources, and to detect the presence of the alkali or alkaline earth elements or various band systems.

The Hartridge Reversion Spectroscope (Beck) splits the spectrum into two halves, one reversed in dispersion to the other. An adjustment makes it possible to shift one half with respect to the other, until a particular absorption band lines up in both spectra, when the wavelength of the band can be read from a wavelength drum. The instrument is used widely in biological and clinical work to identify substances with strong and distinctive absorption bands, such as carbon monoxide.

High dispersion spectroscopes have been



(Courtesy Société Générale d'Optique, Paris, France)

FIG. 9. The Huet industrial spectroscope for comparing the spectrum from an unknown sample with that of standard specimen.

applied extensively to identification of various metallic alloys, particularly for sorting mixed stocks. The first instrument of this kind, the Steeloscope (Hilger & Watts), is shown in Fig. 8. It employs a train of three 60° prisms examined by a 20X eyepiece, to give an apparent dispersion of ap-

proximately 5 Å/mm at 4300 Å, so that even a stainless steel spectrum is well resolved. Later, more sophisticated designs have been developed by Fuess and Société Générale d'Optique (Fig. 9). The Russians used the Hilger Steeloscope extensively to identify and sort the metals recovered from German tanks and other weapons destroyed on the Eastern Front during and after World War II, and have since developed their own designs. With such instruments, mixed stock in a warehouse or scrap yard can be sorted at the rate of 30–100 samples/hour, depending on bulk, similarity and operator proficiency. With care, a quantitative precision of 25–100% can be achieved.

REFERENCES

1. AMICI, G. B., *Museo Fiorentino*, 1, 1 (1860).
2. ZENGER, K. W., *Zeits. f. Instrkde*, 1, 263 (1881).
3. WERNICKE, W., *Zeits. f. Instrkde*, 1, 355 (1881).

R. F. JARRELL

WEATHER EFFECTS ON ACCURACY, *See*
ACCURACY IN SPECTROCHEMICAL
ANALYSIS, p. 99.

ZEEMAN EFFECT*

This effect, named for its discoverer, who observed the first experimental indication of it in 1896, is the splitting of a spectral line into a number of components when the emitting source is placed in a magnetic field. The effect arises, of course, from the splitting of the levels involved in a transition. The explanation has as its starting point Larmor's theorem, which states that the orbital motion of an electron is expected to precess about the axis representing the direction of the magnetic field with uniform angular velocity represented by $\omega_L = H(e/2mc)$, which is the product of the field strength by the ratio between the magnetic moment and

the orbital angular momentum. In the general case it is assumed that more than one electron is involved and that the angular momentum vectors L and S are resultants. Only LS -coupling will be considered in this discussion. In this case the total resultant angular momentum vector, J , precesses about the direction of H , it being assumed that the field is not strong enough to break the coupling between L and S , and thereby causes these vectors to precess independently. This is a simple extension of the treatment where we have a single electron with quantum vectors s and l . When electron spin, which accounts for multiplet structure, is introduced, it becomes necessary to introduce a factor g into the expression for the angular velocity of precession leading to $\omega_L = Hg(e/2mc)$. The g factor, which is equal to the ratio between the total magnetic moment of the atom and the total mechanical moment in units of

$$h/2\pi, \text{ is } g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{J(J+1)}$$

The total energy of the precession is equal to the product of the precessional angular velocity by the component of the resultant mechanical moment projected on the axis of H . This energy which is expressed as an increment to the energy of an unaffected level is

$$\Delta W = M \cdot g \cdot H \cdot \frac{h}{2\pi} \cdot \frac{e}{2mc},$$

in which M is the magnetic quantum number. The part of this expression included in $h/2\pi \cdot e/2mc$ is the Bohr magneton or unit of magnetic moment. To express this energy in wave numbers we divide ΔW by hc and obtain for the separation of the Zeeman component of a level from the unaffected position

$$\Delta \nu = M \cdot g \cdot H \cdot \frac{e}{4\pi mc^2}$$

The expression $He/4\pi mc^2$ is the formula obtained in a classical derivation by Lorentz for

* The sixth in a consecutively developed series of articles on the fundamentals of Optical Emission Spectra: see *Introduction-Designation and Description of Spectra* for list of topics, p. 202.

the separation of the outer component of the triplet from the central component in the so-called normal Zeeman effect. It is called the Lorentz unit, designated L , and is equal to $4.67 \times 10^{-5} \cdot H \text{ cm}^{-1}$. We may then write the formula.

$$\Delta\nu = M \cdot g \cdot L \text{ cm}^{-1}$$

The usual situation giving rise in general to a more complex pattern has been called "anomalous Zeeman effect" for historical reasons. This is somewhat misleading. The patterns are quite regular and predictable with LS coupling and field strengths below a critical value.

To explain the structure of a Zeeman pattern, it is noted that in a magnetic field the total angular momentum J splits into $2J + 1$ components. The values of M may be thought of as the projections of these components of J on the magnetic axis and take values differing from each other by unity from $M = +J$ to $M = -J$. The formation of a pattern is best explained by an example for which we choose $^2S_{1/2} - ^2P_{1/2}$. The appropriate g values are calculated from the formula. Let us arrange the M values for $J = 1\frac{1}{2}$ in a horizontal row with the corresponding Mg products below. Similarly let us arrange the M and Mg values for $J = \frac{1}{2}$ with the Mg values on the line adjacent to those in the previous array:

$$\begin{array}{ccccccc}
 ^2P_{1/2} & M & -1\frac{1}{2} & -\frac{1}{2} & +\frac{1}{2} & +1\frac{1}{2} & \\
 & Mg & -\frac{3}{8} & -\frac{1}{8} & +\frac{1}{8} & +\frac{3}{8} & g = \frac{4}{3} \\
 & & \swarrow & \downarrow & \downarrow & \swarrow & \\
 ^2S_{1/2} & Mg & & -\frac{3}{8} & +\frac{3}{8} & & g = 2 \\
 & M & & -\frac{1}{2} & +\frac{1}{2} & &
 \end{array}$$

The transitions permitted by the selection rule for M , namely $\Delta M = 0, \pm 1$, are shown by the arrows. The resulting pattern is given by

$$\Delta\nu = [(\pm\frac{1}{8}), \pm\frac{3}{8}, \pm\frac{5}{8}] L \text{ cm}^{-1}$$

This is the pattern that appears when observation is at right angles to the field. The

components, shown in parentheses, corresponding to the vertical transition are polarized parallel to the direction of the field and are called p components. Those corresponding to the diagonal transitions are polarized normal to the field and are called s components. For an array such as that shown where the J 's are unequal, the vertical differences at the center and the diagonal differences at the end are the stronger. Where the J 's are equal, giving what is called a "box model," the diagonal differences in the middle and the vertical differences at the end are stronger. In the instance of singlets, $S = 0$ and g reduces to 1. For these cases, if we take the selection rule for M into account, a normal triplet is obtained. An important fact to be noted is that the pattern is unique for a transition associated with a given set of quantum numbers.

A very large number of possible regular patterns were published by Kiess and Meggers.¹ Complete tables of g values for LS coupling are given in "Atomic Energy Levels" and in the "American Institute of Physics Handbook." Formulas are available for other types of coupling or in instances of hyperfine structure.

If the field strength surpasses a critical value the pattern becomes distorted and finally approaches a form in which the entire multiplet approaches the configuration of a normal triplet. This is called the Paschen-Back effect and is caused by the decoupling of the L - and S -vectors, which in the complete development of the effect precess independently around H .

An effect similar to the splitting of spectral by a magnetic field is the Stark effect produced by an electric field, named for its discoverer, and first observed in 1913. The first theoretical explanation of this effect by Schwarzschild and by Epstein was one of the important early successes of the Bohr theory. The detailed experimental observation of the effect is difficult. As it ordinarily manifests itself, the Stark effect causes a line

FLAME PHOTOMETRY

broadening resulting from the fields present in radiation sources.

REFERENCES

1. KIESS, C. C., AND MEGGERS, W. F., *J. Res. NBS*, **1**, 641 (1928).

2. MOORE, CHARLOTTE, E., *Circ. Natl. Bur. Stand.* 467, I (1949); II (1952); III (1958).
3. "American Institute of Physics Handbook," McGraw-Hill, New York (1957).

C. J. HUMPHREYS

FLAME PHOTOMETRY

Flame photometry is the utilization of a flame excitation source in the optical emission spectroscopic analysis of alkali metals, alkaline earth metals and many other elements with excitation potentials low enough for flame excitation.

The first use of the flame as a spectroscopic source is generally attributed to Bunsen and Kirchhoff in 1860 but the relation between chemical composition of substances added and the color of the resulting flame was reported as early as 1862.⁶ Its use was not extensive until after 1945 when commercial flame photometric instrumentation was developed. Now a bibliography¹ containing over 900 references, several books²⁻⁴ and chapters in books^{5, 6} indicate the wide acceptance of flame photometry as an analytical technique.

For analysis with the flame photometer, a sample in solution form is atomized into a flame, and chemical elements contained in the sample are vaporized and excited to emit characteristic electromagnetic radiation—light rays. This light is deflected into a selective filter, a prism or a diffraction grating so that only a narrow portion of the spectrum is separated and directed onto a suitable detector for measuring light intensity. The detector converts the light into electrical energy which is measured with a galvanometer or recorder.

For introduction of the sample solution into the flame, two types of atomizers are used. One type is an integral, atomizer-

burner constructed so that sample solution is injected directly into the flame.^{2a} Another type has a spray chamber where larger droplets condense and finer droplets are swept on into the flame.^{2b} The latter type of atomizer is subject to more matrix errors and is hazardous to use with organic solvents.

Flames used for excitation burn fuel mixtures varying from natural gas-air at a temperature of 2200°K to cyanogen-oxygen at 4800°K.⁷⁻¹¹ Hydrogen-oxygen is generally most useful because it has a sufficiently high temperature, 2900°K, to excite many elements and gives low background emission.

Instruments using light filters, photometers, are adequate for routine analysis or special problems but are usually limited by interference from spectral overlap and because they are less flexible for nonroutine use. Modern filters such as interference filters can now be obtained which transmit very narrow light bands, thereby minimizing spectral overlap. Instruments using prisms or diffraction gratings, spectrophotometers, are preferred because of the much wider variety of elements they can detect.^{2c, 5a}

For detecting the emitted light, flame photometers often use barrier-layer cells and, therefore, have less sensitivity. Flame spectrophotometers use phototubes or photomultipliers. Photomultipliers give far greater sensitivity, allowing the use of narrower slits, and, consequently, increasing the ratio of line to background light and lowering detection limits.^{2d}

For measuring instrument response, galvanometers are generally used, although recorders are becoming more popular because they offer several advantages. They can be employed to smooth out flame fluctuations, they are easier to read, and they can be used in conjunction with a wavelength scanning device to record spectra.¹²⁻¹⁴

Quantitative determinations with the flame photometer are very rapid and precise. A single measurement for a sample solution can be made in ten seconds and can be repeated with a precision as good as ± 0.2 per cent of the emission obtained.¹⁵ Because flame photometric methods are empirical, calibration curves must be prepared by plotting the net emission of light versus concentrations of the element to be determined.

Although precision of measurements is excellent, certain errors may be encountered which can lead to inaccuracy.^{2a, 5b, 6a, 15, 16} These errors are caused by differences between the composition of samples and standards. In order to compensate for such errors, several different techniques are in use. One of these techniques, the use of internal standards, is to add a known concentration of an element not present in the sample to both standards and samples. The effect of foreign substances on element emission and variations in the flame theoretically have the same effect on the desired element and the internal standard. Plotting the ratio of light emitted by the sample element and the internal standard element against concentration then compensates for interferences. Instruments have been designed specifically for using internal standards by utilizing simultaneous beams of light coming from the sample element and the internal standard.

The use of internal standards, however, is not always foolproof and may give only partial corrections. For this reason, many analysts prefer to use instruments utilizing a single beam of light and compensate for errors in other ways. Compensations for errors depend on the type of errors, but are pre-

dominantly based on the idea of making samples and standards as nearly identical as possible.

Applications have been mostly for determining sodium and potassium in a wide variety of samples, but are becoming broader as time progresses.¹ Flame photometry became more practical and popular in the United States during and shortly after World War II, when commercial instrumentation was improved. Since then it has developed markedly so that now over sixty elements, including the rare earths, can be detected.¹⁷ Practical determinations are usually limited to fewer elements such as the alkali and alkaline earth metals, boron, chromium, cobalt, copper, iron, lead, manganese, nickel and silver.

Problems limiting practical determinations are gradually being solved with the advent of new developments.⁸ One of these developments is the use of a high-temperature flame,⁸⁻¹¹ such as that produced by burning a mixture of cyanogen and oxygen, which provides for excitation to higher energy levels, producing more atomic spectral lines. Another is chelation and selective extraction with organic solvents.^{18, 19} This can increase sensitivity by concentrating the elements and enhancing its emission. This enhancing effect is caused mainly by the heat contributed to the flame by the solvent. Other improvements resulting in better line to background ratio and/or smaller flame fluctuations will also broaden flame photometric determinations and extend the already significant importance of flame photometry.

REFERENCES*

1. MAVRODINEANU, R., "Bibliography on Analytical Flame Spectroscopy," *Applied Spectroscopy*, **10**, 2-28, Nos. 2 and 3 (1956).
2. BURRIEL-MARTÍ, F., AND RAMÍREZ-MUÑOZ, J., "Flame Photometry", Elsevier Publish-

* The references given here are not complete but were selected so that complete coverage can be obtained by additional references contained in those given.

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- ing Co., Amsterdam, 1957; translated from the original Spanish manuscript by W. C. Darwell. (909 references.)
- 2-a. *Ibid.*, pp. 59-60 (also gives additional references).
- 2-b. *Ibid.*, pp. 52-58 (additional references).
- 2-c. *Ibid.*, pp. 108-135 (comprehensive descriptions of instrumentation).
- 2-d. *Ibid.*, pp. 89-97 (additional references).
- 2-e. *Ibid.*, pp. 174-209 (additional references).
3. HERRMAN, R., "Flame Photometry", Springer Verlag, Berlin-Göttingen-Heidelberg, 1956; in German.
4. MAVRODINEANU, R., AND BOITEUX, H., "Quantitative Spectral Analysis by the Flame", Masson et Cie, Paris, 1954; in French.
5. GARDINER, K. W., Flame Photometry. In "Physical Methods in Chemical Analysis", (Editor W. G. Berl), Vol. III, Academic Press Inc., N. Y., p. 219-280, 1956.
- 5-a. *Ibid.*, p. 243 (Table II lists commercial instruments).
- 5-b. *Ibid.*, pp. 248-274 (additional references).
6. MARGOSHES, M. AND VALLEE, B. L., Flame Photometry and Spectrometry. Principles and Applications. In "Methods of Biochemical Analysis". (Editor David Gliek), Vol. III, p. 353-407. Interscience Publ., N. Y., 1956.
- 6-a. *Ibid.*, pp. 372-384 (additional references).
7. LIBBY, W. F., *Chem. Eng. News* (July 16, 1956), 3442 (illustrated table of flame temperatures).
8. GILBERT, P. T., JR., "Analytical Flame Photometry: New Developments, American Society For Testing Materials," Spectroscopy Symposium, San Francisco, California, October 13, 1959 (Table I lists various flame temperatures and references).
9. GILBERT, P. T., JR., "Oxycyanogen Flame Photometry," Pittsburgh Conference on Anal. Chem. and Appl. Spectroscopy, Pittsburgh, Pa., Mar. 6, 1958.
10. VALLEE, B. L., AND BARTHOLOMAY, A., *Anal. Chem.*, **28**, 1753 (1956).
11. FUWA, KEIICHIRO, THEIRS, R. E., AND VALLEE, B. L., *Anal. Chem.*, **31**, 1419 (1959).
12. KING, W. H., JR., AND PRIESTLEY, W., JR., "A Modified Recording Flame Photometer, Am. Soc. Testing Materials," Symposium on Flame Photometry, Spec. Techn. Publ. No. 116, 97 (1951).
13. WATANABE, H. AND KENDALL, K. K., JR., "Flame Spectrograms I. Common Metals," *Appl. Spectroscopy*, **9**, 132 (1955).
14. WHISMAN, M. AND ECCLESTON, B. H., "Flame Spectra of Twenty Metals Using a Recording Flame Spectrophotometer," *Anal. Chem.*, **27**, 1861 (1955).
15. BECKMAN INSTRUMENTS, INC., Bull. 259.
16. FOSTER, W. H., JR., Ph.D. Thesis, M.I.T., May, 1959.
17. GILBERT, P. T., JR., Beckman Bulletin 753, 1959.
18. DEAN, J. A., Use of Organic Solvents in Flame Photometry, "Symposium on Solvent Extractions in the Analysis of Metals", Am. Soc. Testing Materials, Spec. Tech. Publ. No. 238, 43-54, 1958.
19. LADY, J. H., Ph.D. dissertation, University of Tennessee, Aug. 1955.

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ALLOYS

Flame photometry is valuable in the analysis of metallurgical alloys when a simple, reasonably accurate, and rapid method of analysis is required. Compared with an arc or a spark source, flames excite fewer lines of each element—an advantage; also sample introduction and excitation conditions are less difficult to establish. Flame methods should be of interest to small foundries which do not have spectrographic facilities, as well as for production and control laboratories.

Necessary equipment includes a quartz-prism or grating monochromator equipped with adjustable entrance and exit slits, an aspirator-burner combination employing an oxygen-hydrogen or an oxygen-acetylene flame, and separate blue- and red-sensitive photomultiplier receptors with associated electronic amplifier. Recording attachments are desirable.⁸

Solvent extraction,^{6,7} followed by aspiration of the organic phase into the flame, is being used to an increasing extent. Intensification of emission intensities ranging from ten- to twenty-fold is usual. The increased emission intensity allows greater resolution and enables less concentrated samples to be analyzed without any loss in precision. By lowering the concentration levels of matrix elements, or by selective extraction of test

elements from other matrix elements, spectral and radiation interferences may often be circumvented.

Studies with very high temperature sources, such as the oxygen-cyanogen flame, and the development of absorption flame methods offer promise for the determination of elements which are not excited to emission in an oxygen-hydrogen or an oxygen-acetylene flame.

As a guide to the application of flame photometry for alloy analysis, methods for constituents in various classes of sample material will be outlined in the following sections. Detailed procedures will be found in the references cited. A thorough discussion for each element, which includes the spectrum excited to emission, optimum excitation conditions, and spectral and radiation interferences from other cations and anions, is available and should be consulted.⁹

Ferrous Alloys

Alkali and Alkaline Earth Metals.

Kuettel and Karl²⁹ have determined calcium, lithium, magnesium, and sodium in ductile cast iron and nodular iron. The method is applied after a preliminary extraction of iron with ether. Solutions, prepared from samples 4-grams in weight, were diluted to a final volume of 50 ml. Phosphorus is the only element causing interference in considerable magnitude; compensation is effected by using standards prepared from pure cast iron with a phosphorus content within 0.02% that of the samples. Known amounts of the test elements are added to these solutions. The method of standard addition would be more convenient perhaps.

Abresch and Dobner¹ have discussed their experience with flame methods in the determination of calcium and magnesium in the steel-plant laboratory.

Aluminum. To determine acid-soluble aluminum, Eshelman *et al.*¹⁵ removed the iron from aliquots containing between 0.1 and 0.5 mg. of aluminum by extraction with

4-methyl-pentan-2-one from a 5*M* hydrochloric acid solution. The aqueous phase was evaporated to incipient dryness, dissolved in a few milliliters of water, and the aluminum extracted with cupferron from an acetate solution adjusted to pH 2.5 to 4.5 with a known volume of 4-methyl-pentan-2-one. One 3-minute shaking removes all the aluminum. The organic phase is aspirated directly into the flame and the emission intensity of the line at 396.2 m μ , or of the band head at 484 m μ , is compared with standards prepared by a similar cupferrate extraction of aluminum aqueous standards. Sensitivity is 0.2 μ g of aluminum per ml. per scale division (%*T*-scale).

Chromium. Bryan and Dean⁸ selectively extracted chromium(VI) with 4-methyl-pentan-2-one from an aqueous solution 1*M* in hydrochloric acid and maintained at 0° to 10°C. Shaking for one minute is sufficient. The organic phase is aspirated directly into the flame. Although some iron accompanies chromium in the extraction, it does not interfere with the chromium lines at 359.4 and 425.4 m μ . Furthermore, a single backwash of the organic phase with fresh 1*M* hydrochloric acid removed 97 per cent of any iron extracted and permitted several tenths of a gram of iron to be present in the initial aqueous phase. Emission sensitivity is 0.1 μ g of chromium per ml. per %*T*. The method has been applied to many types of steel and cast iron samples, some with a chromium content as low as 0.029%.

Less successful are the direct methods employed by Burriel-Marti *et al.*⁴ and by Ikeda.²⁷

Copper. The direct determination of copper is subject to serious interferences with some types of ferrous alloys; however, organic solvent extraction has been successfully employed by Dean and Lady.¹² Fifteen to 150 micrograms of copper, in the form of the salicylaldoxime complex, is selectively extracted from the aqueous solution of the sample with four successive 5-ml. portions of

chloroform or *n*-amyl acetate. Citrate is employed to buffer the solution at pH 3 and to mask the iron(III) and thereby to prevent its coextraction. The copper emission is measured at 324.7 $m\mu$.

Ferrite Composition of Steels. Wever, Koch and Wiethoff³⁵ isolated electrolytically the carbides in chromium-manganese steels and determined the chromium-manganese-iron content of the ferrite dissolved in the citrate electrolyte. Standards of each of these elements were prepared in a similar citrate solution.

Manganese. On aliquots of stainless steel samples containing less than 100 ppm of manganese, Dippel and Bricker¹⁴ successfully employed the method of standard addition to determine the manganese content and to overcome the serious inhibition of other sample components. The method of Burriel-Martí *et al.*⁴ necessitates the use of numerous correction curves to overcome similar interferences.

Nickel and Cobalt. No satisfactory method has been reported for these elements where emission lines seriously overlap each other except for the cobalt line at 387.3 $m\mu$ and the nickel line at 361.9 $m\mu$. Burriel-Martí *et al.*⁴ precipitated nickel with dimethylglyoxime, extracted with chloroform, stripped the organic phase with 5*M* hydrochloric acid, and measured the nickel emission on the acid-strip solution. The back-extraction sacrifices the intensification obtained with the use of organic solvents.

It should be possible to determine cobalt and nickel by the use of suitable organic solvent-extraction methods following removal of the bulk of the iron.^{10, 15, 19}

Nonferrous Alloys

Aluminum-base Alloys. *Chromium.* The method outlined under ferrous alloys is suitable. There are no interferences.

Copper. The sample is simply dissolved and atomized directly into the flame. The copper emission is read at 324.7 $m\mu$.⁵

Dean and Cain¹⁰ selectively extracted copper, manganese, and nickel (plus any cobalt) as the diethyldithiocarbamates from a citrate-buffered solution with chloroform. The organic phase was aspirated into the flame and the emission intensity of each element was measured at 324.7, 403.3, and 352.5 $m\mu$, respectively.

Gallium and Indium. The sample is dissolved and aspirated directly. Indium is read at 451.1 $m\mu$.³¹ The method reported for gallium by Meloche and Beck³⁰ should be applicable to aluminum alloys. The emission is read at 417.2 $m\mu$.

Iron. Dean and Lady¹¹ extracted a sample, adjusted to pH 0.5, with six successive portions of acetylacetone. Later work by the author and unpublished studies by Menis and Rains have shown that a single extraction with 4-methyl-pentan-2-one from a solution 5*M* in hydrochloric acid is sufficient to remove the iron quantitatively. With either solvent, the organic phase is aspirated into the flame and the iron read at 372.0 or 386.0 $m\mu$.

Magnesium. The sample is dissolved and aspirated directly. The crests of the molecular band systems are measured at 372 or 383 $m\mu$. Standards should contain equivalent amounts of aluminum and acid, but other constituents exert no effect.²⁵

Manganese. Dippel and Bricker¹⁴ employed the standard-addition method to evaluate the manganese content on dissolved samples without any prior separations. Manganese is read at 403.3 $m\mu$. See also the extraction method described under "Copper."

Sodium. The dissolved sample is aspirated directly and the sodium emission is read at 589 $m\mu$. Standards should contain equivalent amounts of aluminum and copper.²³ The acid concentration is not particularly critical, but should not exceed certain limits.²⁴

Copper- and Nickel-base Alloys. For aluminum, the method described under "Ferrous Alloys" is suitable after removal of the copper (or nickel) by a mercury-cathode separation.

For chromium and iron, the method outlined under "Aluminum Alloys" is suitable.

For manganese, the method described under "Ferrous Alloys" is suitable.

Magnesium-Lithium Alloys. For lithium, Strange³⁴ has described a method for the range 1 to 10 per cent; Robinson and Ovenston,³² for the range 11 to 14 per cent. To compensate for the suppressing effect of magnesium and aluminum, addition of these elements to the standard solutions is recommended. The latter authors used a double-beam instrument and added 1600 ppm of potassium at internal standard and quantities of acid similar to those employed to dissolve the sample.

Tin-base Alloys. Generally it is difficult to prevent extensive hydrolysis with the amounts of tin normally present. Consequently, tin, along with any antimony and arsenic, is removed by volatilization of the bromides. Copper is determined directly on the residual sample.⁵

Zinc-base Alloys. After zinc is removed as the diethyldithiocarbamate in a preliminary extraction with chloroform, aluminum is determined by extraction with a 0.1*M* solution of 2-thenoyltrifluoroacetone (TTA) in 4-methyl-pentan-2-one.¹⁵ The organic phase is aspirated into the flame and the aluminum measured at 396.2 or 484 $m\mu$.

Copper is determined directly on the original aqueous solution.⁵

For iron, the method described under "Aluminum alloys" is suitable.

Essentially Pure Metals

Generally analyses of this type have been confined to the determination of alkali metals in various "pure" metals: sodium in aluminum,^{3, 23, 24} in lead,¹⁷ in lithium,²⁸ and in tungsten²²; and of potassium in aluminum,³⁸ in lithium,²⁸ in lead,³⁸ and in tungsten.²² Standards are prepared from the respective pure metal to which are added varying amounts of the test element. When necessary, the standard-addition method may be

employed to ascertain the quantity of test element present in the metals used for preparation of the standard solutions.

Cadmium. The amount of cadmium metal plated on small cylinders of aluminum was determined by Gilbert²⁰ using the cadmium line at 326.1 $m\mu$.

Cobalt. Galloway¹⁹ has determined cobalt, copper, and iron in cobalt mattes and concentrates. Samples, 0.1-gram in weight, are dissolved in the usual manner. The solution, 8*M* in hydrochloric acid, is extracted with two portions of an ethyl methyl ketone-chloroform (2 + 1) mixture. The iron extracts are combined and back-washed with a fresh 8*M* acid solution. The organic phase could be aspirated directly or else the solvent is removed by evaporation, organic matter destroyed, and the residual salts dissolved in water. Iron is measured at 386.0 $m\mu$.

The aqueous layers are combined, heated to remove residual organic solvent, and concentrated to about 5 ml. Ten ml. of isopropyl alcohol is added and the solution is diluted to 100 ml. with water. Cobalt is read at 387.3 $m\mu$ and copper at 324.7 $m\mu$.

Copper. Galloway¹⁸ has determined silver in blister copper by precipitation of silver as the chloride, dissolving by successive treatments with aqueous ammonia and hot nitric acid, and measuring the silver in the resulting solution at 338.3 $m\mu$. None of the common metals interfere.

Nickel. Yokosuka³⁶ has determined calcium in metallic nickel. The nickel is removed by a mercury-cathode separation, along with other minor constituents of the sample, and any aluminum present is extracted as an 8-quinolinolate at pH 9. The residual solution is evaporated to dryness, the residue dissolved in *N* hydrochloric acid, 40 volume per cent of methanol is added, and the calcium emission is measured.

Related to the topic of alloys is the analysis of plating solutions. Fornwalt,¹⁶ following the method of Dean and Thompson,¹⁸ employed 50 volume per cent methanol-wa-

ter solutions for the determination of boron in nickel plating baths. Readings are taken at the 518-m μ or the 546-m μ band heads and corrections applied for the flame background emission by taking a reading at the minimum on either side of the crests. The nickel concentration is determined in the same solution by taking readings at 352.5 m μ .

Tungsten. In addition to the determination of sodium and potassium in tungsten metal and tungsten ores mentioned earlier, calcium has also been determined by the same investigators²² and in the same general manner.

Indium. Gilbert²¹ handled quantities of indium which corresponded to a film evaporated onto supporting surfaces. Readings were made at 451.1 m μ .

REFERENCES

1. ABRESCH, K., AND DOBNER, W., *Arch. Eisenhüttenw.*, **29**, 25 (1958).
2. BREWSTER, D., AND CLAUSEN, C., *Iron Age*, **166** (No. 18) 88 (1950).
3. BRYAN, H. A., AND DEAN, J. A., *Anal. Chem.*, **29**, 1289 (1957).
4. BURRIEL-MARTÍ, F., RAMÍREZ-MUÑOZ, J., AND ASUNCION-OMARREMENTERIA, M. C., *Mikrochim. Acta* (1956) 362.
5. DEAN, J. A., *Anal. Chem.*, **27**, 1224 (1955).
6. DEAN, J. A., *Am. Soc. Testing Materials, Spec. Tech. Publ.* **238**, 43 (1958).
7. DEAN, J. A.: "Flame Photometry," Chap. 5, McGraw-Hill Book Company, New York, 1960.
8. DEAN, J. A., *Op. cit.*, Chap. 6.
9. DEAN, J. A., *Op. cit.*, Chaps. 11 to 19.
10. DEAN, J. A., AND CAIN, C., *Anal. Chem.*, **29**, 530 (1957).
11. DEAN, J. A., AND LADY, J. H., *Ibid.*, **27**, 1533 (1955).
12. DEAN, J. A., AND LADY, J. H., *Ibid.*, **28**, 1837 (1956).
13. DEAN, J. A., AND THOMPSON, C., *Ibid.*, **27**, 42 (1955).
14. DIPPEL, W. A., AND BRICKER, C. E., *Ibid.*, **27**, 1484 (1955).
15. ESHELMAN, H. C., DEAN, J. A., MENIS, O., RAINS, T. C., *Ibid.*, **31**, 183 (1959).
16. FERNWALT, D. E., *Anal. Chim. Acta*, **17**, 597 (1957).
17. FUKUSHIMA, S., IWATA, S., KUME, S., AND SHIGEMOTO, M., *Japan Analyst*, **5**, 704 (1956).
18. GALLOWAY, H. McN., *Analyst*, **83**, 373 (1958).
19. GALLOWAY, H. McN., *Ibid.*, **84**, 505 (1959).
20. GILBERT, P. T., *Anal. Chem.*, **31**, 110 (1959).
21. GILBERT, P. T., *Spectrochim. Acta*, **12**, 397 (1958).
22. HEGEDUS, A. J., NEUGEBAUER, J., AND DOVORSZKY, M., *Mikrochim. Acta*, 282 (1959).
23. HOURIGAN, H. F., AND ROBINSON, J. W., *Anal. Chim. Acta*, **13**, 179 (1955).
24. IKEDA, S., *Science Reports Research Insts., Tohoku Univ.*, **7A**, 29 (1955).
25. IKEDA, S., *Ibid.*, **8A**, 9 (1956).
26. IKEDA, S., *Ibid.*, **8A**, 449 (1956).
27. IKEDA, S., *Ibid.*, **8A**, 463 (1956).
28. INMAN, W. R., ROGERS, R. A., AND FOURNIER, J. A., *Anal. Chem.*, **23**, 482 (1951).
29. KUEMMEL, D. F., AND KARL, H. L., *Ibid.*, **26**, 386 (1954).
30. MELOCHE, V. W., AND BECK, B. L., *Ibid.*, **28**, 1890 (1956).
31. MELOCHE, V. W., RAMSAY, J. B., MACK, D. J., AND PHILIPS, T. V., *Ibid.*, **26**, 1387 (1954).
32. ROBINSON, A. M., AND OVENSTON, T. C. J., *Analyst*, **79**, 47 (1954).
33. RUSANOV, A. K., AND BODENKOV, B. I., *Z. anal. Chem.*, **106**, 419 (1936).
34. STRANGE, E. E., *Anal. Chem.*, **25**, 650 (1953).
35. WEVER, F., KOCH, W., AND WIETHOFF, G., *Arch. Eisenhüttenw.*, **24**, 383 (1953).
36. YOKOSUKA, S., *Japan Analyst*, **5**, 71 (1956).

JOHN A. DEAN

CYANOGEN

Recent investigations have shown that the cyanogen-oxygen flame has properties which make it an excellent source in flame photometry. Because the products of combustion are extremely stable and the reaction is highly exothermic, the temperature of the cyanogen-oxygen flame is very high. This high temperature causes excitation of many elements not readily excited by ordinary flame sources. It is the purpose of this article to summarize some of the developments leading to the use of this flame as a source in spectrochemical analysis and to cover the recent work on cyanogen flame photometry.

History and Development. Dixon⁴ first attempted to determine the temperature of

the cyanogen-oxygen flame using a method involving the speed of sound through the flame gases. He found the temperature to be approximately 4200°K. Various spectroscopic measurements including measurement of rotational,⁹ vibrational⁹ and translational⁸ spectra also showed an extremely hot flame, although no reliable values for the temperature were obtained.

The most accurate means of measuring flame temperatures appears to be the line-reversal method.⁷ In this method the spectrum of a controllable continuous source is viewed through the flame. A small amount of a metal salt, e.g., sodium chloride, is added to the flame, and the background source is adjusted until the spectrum line of neither the emission nor the absorption spectra of the flame appears against the background. The background source is then assumed to have the same temperature as the flame. Conway, Wilson and Grosse⁸ modified the line-reversal method to allow the use of the sun as background source. A variable absorbing agent was used to control the amount of the sun's radiation used as background. By this method the flame temperature for a 1:1 molar mixture of cyanogen and oxygen was found to be approximately 4650°K. This compares favorably with the theoretical value of 4835°K calculated from thermodynamic data.²

Analytical Applications. Baker and Vallee,¹ in a brief examination of the use of the cyanogen flame as a source in flame photometry, detected emission lines for Ag, Al, Ba, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Sr using a short exposure time and a small amount of sample. None of these emission lines could be detected with the hydrogen-oxygen flame under identical excitation conditions. This was used to demonstrate the greater sensitivity of the cyanogen flame.

The above elements have since been successfully determined quantitatively by Vallee and Bartholomay.¹⁰ A recently developed burner^{5,6} should add to the efficiency of the

flame and consequently to the utility of the method.

Cyanogen flame photometry is not fully developed at the present time, but it shows promise of becoming a useful tool for the quantitative determination of small concentrations of metals with high excitation potentials. Advantages of cyanogen-oxygen over more commonly used fuels include increased sensitivity for the determination of many elements of high excitation potential and lessened anion interferences.

REFERENCES

1. BAKER, M. R., AND VALLEE, B. L., *J. Opt. Soc. Am.*, **45**, 773 (1955).
2. CONWAY, J. B., SMITH, W. F. R., LIDDELL, W. J., AND GROSSE, A. V., *J. Am. Chem. Soc.*, **77**, 2026 (1955).
3. CONWAY, J. B., WILSON, R. H., GROSSE, A. V., *J. Am. Chem. Soc.*, **75**, 499 (1953).
4. DIXON, H., *Ber. dtsch. chem. Ges.*, **38**, 2418 (1905).
5. FUWA, K., THIERS, R. E., AND VALLEE, B. L., *Anal. Chem.*, **31**, 1419 (1959).
6. FUWA, K., THIERS, R. E., VALLEE, B. L., AND BAKER, M. R., *Anal. Chem.*, **31**, 2039 (1959).
7. GAYDON, A. G., AND WOLFHARD, H. G., *Proc. Phys. Soc.*, **65A**, 19 (1952).
8. ORNSTEIN, L. S., AND BRINKMAN, H., *Proc. Acad. Sci. (Amsterdam)*, **34**, 33 (1931).
9. THOMAS, N., GAYDON, A. G., AND BREWER, L., *J. Chem. Phys.*, **20**, 369 (1952).
10. VALLEE, B. L., AND BARTHOLOMAY, A. F., *Anal. Chem.*, **28**, 1753 (1956).

ROBERT P. CLARK

EXCITATION MECHANISM

In the course of studying flame photometry in high temperature flames (oxy-cyanogen—5000°C) and low temperature flames (oxy-hydrogen—3000°C), several interesting observations were made which were not explained by current interpretation of flame spectra. These were as follows:

(1) The flame acts as a U.V. source. The intensity of metal spectra increases with increased U.V. radiation from the flame, even when the temperature of the flame decreases.

FLAME PHOTOMETRY

(2) Metal spectral lines with wavelengths less than 2800Å are not usually observed.

(3) Organic solvents increase the spectral intensity many-fold.

Current theory holds that flame temperature is the main variable in controlling spectral intensity. Although it explains qualitatively the third of these observations, it does not explain the first two.

In an effort to understand these phenomena, several postulations are made. It is proposed that metal atoms are excited by ultraviolet light in the flame and that this means of excitation is at least as important as the temperature of the flame. It is also proposed that the mechanism of attaining this state is dependent on the solvent used (organic or aqueous). Further, it is believed that some of the emitted energy is self-absorbed by the flame. Experimental evidence concerning the validity of these proposals has been obtained.

Evidence concerning the validity of these points is given below.

The Flame Acts as a Source of Ultraviolet Light. Two types of flames were studied: (a) oxy-hydrogen, and (b) oxy-cyanogen. It was found by scanning the U.V. emission spectra of these flames that the intensity of emission could be changed considerably by changing the ratio of fuel to oxygen. It was further observed that the intensity of emission of iron spectral lines excited by these flames increased with increased U.V. light in the flame although the flame was below the maximum temperature in these cases. The results are summarized in the following table.

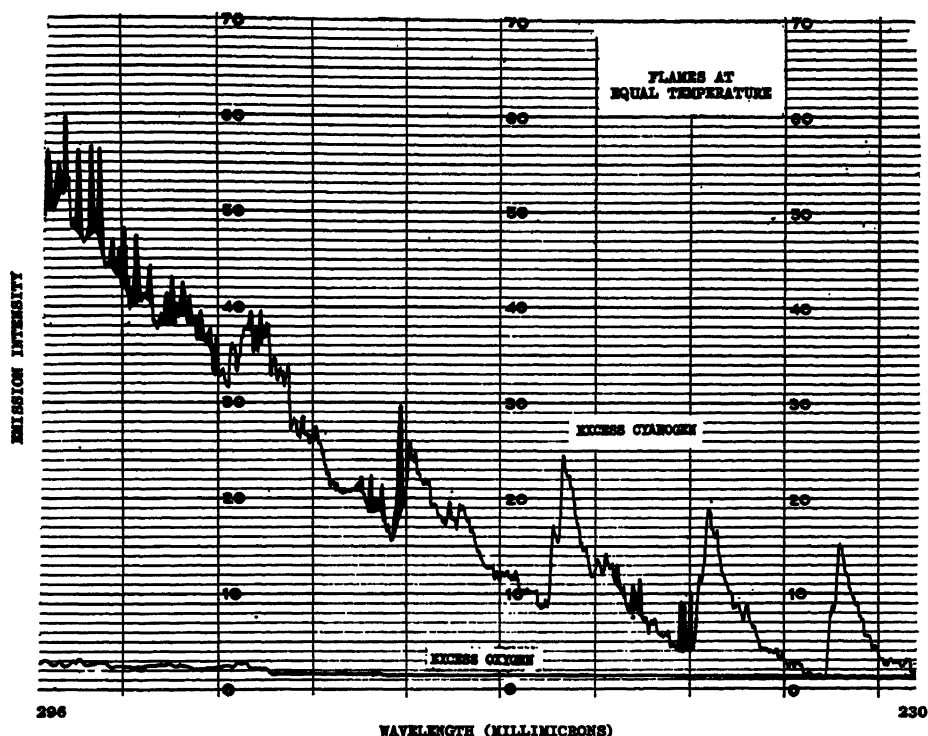
Results indicated increased metal emission with increased U.V. intensity in the flame but not with increased temperature. It should be noted that increased U.V. emission occurred with excess oxygen in the hydrogen flame and excess cyanogen in the second case.

Further evidence for this postulation was obtained when it was observed with the oxy-hydrogen flame that spectral lines with wavelengths below 2800Å were not usually detected although many metals have intense spectrographic lines in this region. It was noted that intense flame emission occurred at 3060Å (water bands) and that metal emission lines with longer wavelengths were usually observed.

If it is conceded that the metals are excited by U.V. light, it is logical that the intense flame radiation at 3060Å is the shortest wavelength excitation source. Wave mechanics tells us that this radiation will excite lines of longer wavelength, but not shorter wavelength. This fits in closely with experimental observation.

More striking evidence in support of this theory is found in Figure 1. This shows the spectra between 2300Å and 3000Å exhibited by oxy-cyanogen flames set at the same temperature. In one flame there was excess oxygen. Very little, if any, U.V. radiation was detected. When iron was atomized into this flame, no spectral lines were observed in this region. The second flame contained excess cyanogen. Since these two flames were at equal temperatures, spectral variation could not be caused by temperature differences. However, this flame exhibited strong U.V.

	Oxy-Hydrogen			Oxy-Cyanide		
	Excess H ₂	Stoichiometric (Hottest)	Excess O ₂	Excess (CN) ₂	Stoichiometric	Excess O ₂
Temperature	Low	Medium	Low	Medium	High	Medium
U.V. Emission (3060Å Water Band)	Medium	Medium	High	High	Low	Low
Fe Emission (3440 Double)	Medium	Medium	High	High	Low	Low



(Esso Research Laboratories, Esso Standard Oil Company Louisiana, Division)

FIG. 1. Spectrum of iron in oxy-cyanogen flame. Iron lines (solid) superimposed on oxy-cyanogen flame spectrum.

Note: Cyanogen flame with excess oxygen generated no U. V. light or iron spectrum although the temperature of both flames was equal.

emission in the range $2300\text{--}3000\text{\AA}$. When iron was atomized into this flame, numerous spectral lines were exhibited as can be seen from Figure 1.

These two flames differ only in their spectral character, their temperatures being equal. It seems likely, therefore, that the difference in excitation of iron spectrum is caused by the difference in U.V. light in the flame.

To summarize, if temperature were the only source of excitation, then all spectral lines, even down to $2000\text{\AA}$ would be excited in a flame. However, we have seen that normally only lines with wavelengths greater than $2800\text{\AA}$ are excited. This coincides with the wavelength of the intense lines found in oxy-hydrogen and oxy-cyanogen flames. Further, when the oxy-cyanogen flame is distorted to

radiate short wavelength U.V. light, then metal emission lines are detected throughout the wavelength band $2000\text{\AA}$ to $2800\text{\AA}$.

Excitation Using an External Source of U.V. Light. If, as has been postulated, spectra can be generated by U.V. light, it should be possible to use an external source of U.V. light to generate spectra. This was examined experimentally in the following manner.

Equipment: A schematic diagram of the equipment is shown in Figure 2.

An aqueous solution of a suitable metal was aspirated into a standard Beckman flame photometer burner. The spectrophotometer was arranged such that the detector continuously monitored the resonance line of the metal being examined. A hollow cathode was positioned at right angles to the

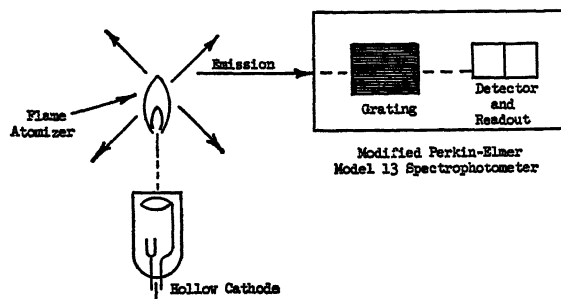


Fig. 2. Equipment used for external excitation of metal spectra.

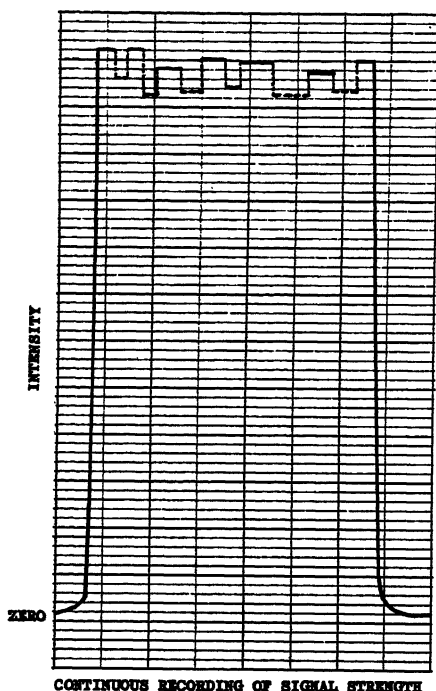


Fig. 3. Enhancement of Mg 2852 Å line using a hollow cathode. — Mg (1000 ppm) with hollow cathode— Mg (1000 ppm) without hollow cathode.

light path of the flame and the slit of the spectrophotometer. The intensity of the emission was measured (a) with the hollow cathode on and (b) with it off. If excitation of the metal atoms in the flame occurs, there should be enhancement of the strength of the spectral line. Of course, it will be appreciated that the metal atoms will absorb the U.V. light and re-emit at random, forming a sphere

of radiant energy. The slit sees a very small part of this sphere and therefore only a very small portion of the re-emitted light would be utilized. To detect this small amount of energy, the instrument was run at maximum sensitivity. The results obtained were as follows:

Sodium. λ 5890 Å. No enhancement of intensity was detected. However, it was noted that the intensity of the flame emission signal was so high that it would be very difficult to detect the small enhancement expected.

Nickel. λ 3524.5 Å, 3414 Å. No enhancement was detected. In this case the oscillator strength of these spectral lines is low. This would mean that the nickel would be very inefficient in absorbing energy from the hollow cathode. As a result, only a small amount of energy would be re-emitted.

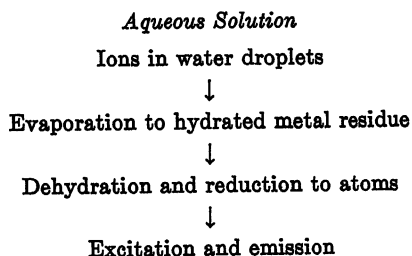
Magnesium. λ 2852 Å. The results obtained with magnesium are shown in Figure 3.

With magnesium, conditions for the detection of "fluoresced" light were good. The intensity of the emission line was low allowing the instrument to be set at high sensitivity. Further, the oscillator strength of the absorption line was high. This permits an efficient absorption of the energy from the hollow cathode. Under these conditions any re-emitted signal was significant compared to the emission of the metal excited by the flame alone. This allowed a significant measurement of "fluoresced" light to be made.

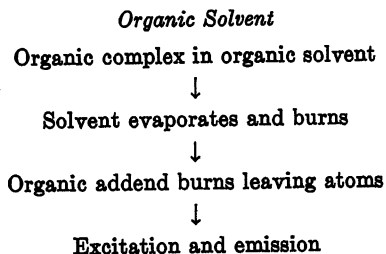
It appears from Figure 3 that some enhancement of the signal occurred. Care was taken to prevent reflected light from the hollow cathode reaching the entrance slit of the monochromator. Further, since there was no enhancement detected in the case of sodium and nickel, it can be assumed that the reflections would have caused an apparent signal in the case of these two metals.

Effect of Type of Solvent. In flame photometry, when organic solvents are used instead of aqueous solvents, a many-fold ($\times 20$) increase in emission intensity occurs. This is explained in part by increased flame temperature, but this cannot completely explain the great increase in sensitivity observed by workers in the field.

Two different processes of excitation are proposed for aqueous and organic solvents which greatly influence the percentage of atoms excited in flame processes. A schematic representation of these processes is as follows:



This is an endothermic process. Many ions will go through the flame without getting excited.



This is an exothermic process and therefore more efficient. Because a greater number of atoms are excited when an organic sol-

vent is used, the emission spectrum is stronger. Further evidence is shown by the observation that in atomic absorption spectroscopy greater *absorption* occurs from metals burned in organic solvents than in aqueous solution.

This fact cannot be explained by increased flame temperature when organic solvents are burned, because increased flame temperature would result in a reduction of the number of atoms in the ground state and hence a decrease in absorption. The proposed mechanism for organic solution results both in more free atoms and more excited atoms.

Wave Mechanics. The intensity of spectral lines is governed by two equations—the Einstein-Boltzmann equation:

$$\frac{N_2}{N_1} = \frac{g_1 e^{-E/kT}}{g_2}$$

and the equation for the strength of spectral line:

$$S = N_2 E = N_1 E \frac{g_1 e^{-E/kT}}{g_2}$$

These equations are correct in themselves but pertain only under black body conditions. A metal in a flame cannot be considered to be under black body conditions because of the U.V. light from the flame. The effect of temperature on the emission spectrum is explained by these equations but not the effect of U.V. emission.

Excitation during Chemical Reaction. The process of forming excited atoms of a metal dissolved in an aqueous or organic solution probably follows the pattern described earlier. During this process, the metal is at one stage combined to form a stable molecule. This may be an oxide, hydroxide, or organic in nature. The fact that the metal is combined indicates that the valence electrons are in a molecular orbit. In order to emit atomic spectra the molecule must be broken down and metal atoms released. This process of producing metal atoms would give rise to the emission spectra of the metal concerned. It

will be remembered that the valence electrons are responsible for the emission of spectra. In a combined atom, the valence electrons are in a molecular orbit. When the molecule is broken down the electron must return to ground state atomic orbits. It is a distinct possibility that the electron changes from a molecular orbit to *excited* atomic orbits and then to the ground state orbit. In this process, the electron would emit atomic spectra when descending from excited atomic orbits. The transfer from molecular orbits would probably be accompanied by emission of unquantized energy. This would account for the high background sometimes associated with emission techniques.

In effect, this would mean that it is possible to use the chemical energy stored in a molecule for the excitation of spectra. No doubt much of the energy required to produce a chemical reaction is stored as potential energy in the valence electrons. When these bonds are broken, the electrons liberate the energy, perhaps in the form of emission, and return to the ground state. The process is therefore a possible explanation of the observation of high energy emission lines in systems which do not have sufficient energy to excite them.

It will be readily understood that the chemical composition of the metal molecule will have a far reaching effect on the efficiency of this process, and on the extent to which various emission lines are excited.

A schematic diagram of this process is shown in Figure 4.

Absorption Effect of Solvent. The absorption effect of solvents or fragments of solvents burning in the flame is an important

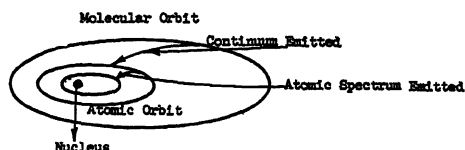


FIG. 4. Production of spectra during chemical reaction. These orbits are not intended to represent actual orbits, merely to represent the process.

variable in the excitation process. Any absorption of the U.V. light in the flame would decrease the excitation of the metal atoms present. It has been observed experimentally that absorption of transmitted U.V. light occurs in the inner cone of the flame. It is reasonable to assume that if transmitted U.V. light is absorbed, then internally generated U.V. light is also absorbed. The solvent, therefore, has an important suppression effect on the intensity of the metal spectra by (a) absorbing U.V. light in the flame and diminishing U.V. excitation of the metals, and (b) by absorbing the spectrum emitted by the excited metal.

Conclusions. It is concluded from these observations that the intensity of a metal emission spectrum is dependent on the following variables:

1. *Efficiency of Producing Atoms.* This is dependent on the solvent and controls the number of ions converted to atoms on passage through a flame.

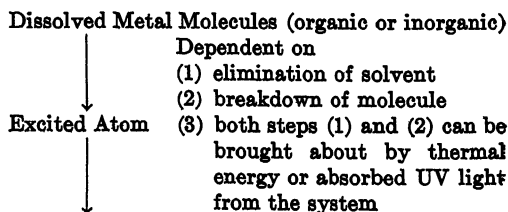
2. *Chemical Reaction.* During the transition of the valence electron from molecular to ground state atomic orbits, quantized (line spectra) and unquantized (background) energy may be emitted.

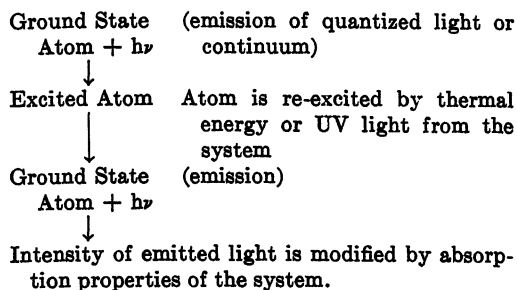
3. *Temperature.* Ground state atoms may be excited by thermal energy. The equation listed above indicates the temperature/emission intensity relationship.

4. *The UV Light Generated in the Flame.* Both the wavelength and intensity of this light is important in exciting spectra.

5. *Absorption of UV Light by Solvents or Fragments of Solvents Present in the Flame.* If the flame absorbs light it may decrease the intensity of emission at certain wavelengths.

This can be summarized as follows:





J. W. ROBINSON

INDIRECT METHOD

Despite the notable success of flame photometry in elemental analysis several of the more common and important elements cannot be determined in this manner because they do not yield characteristic or discrete flame spectra. Among those elements are the halogens, nitrogen, oxygen, and sulfur. Even when arc or spark excitation are utilized to provide much greater excitation energies, only a portion of these elements can be analyzed and then under special conditions. In many instances, however, an indirect procedure can be applied to the determination of these elements whereby the inherent advantages of flame photometry can be retained. A number of indirect flame photometric methods have been developed and further applications should be feasible.

The primary objective of this review is to integrate and bring up to date the information available on indirect flame photometry. This subject is discussed in several texts^{1, 2} and in a current paper by Gilbert.³ Since the information contained in the literature is often incomplete, a certain amount of interpretation is attempted. In general, however, no attempt will be made to systematize information concerning the relative sensitivity and precision of the different methods, since information of this character is rarely presented in a manner amenable to comparison.

Indirect flame photometric methods can be classified into three general groups: (a) those in which spectral measurements are

made of characteristic molecular or radical bands, (b) those involving chemical separations, including precipitation, extraction and ion exchange and (c) methods based on the interference of the element to be determined with the direct flame photometry of another element.

Methods have been developed for the determination of several elements, based on spectral measurements of the characteristic emissivity of molecules or radicals formed in the flame. Nitrogen in 65 nitrogenous compounds was determined by Honma and Smith⁴ by measuring the intensity of a CN band at its peak wavelength of 388.3 $m\mu$. They found the optimum range to be 0.1 to 15 per cent nitrogen and that elemental nitrogen need not be excluded since it does not interfere. The method was not satisfactory for nitrogen in alkali nitrites, nitrates or cyanides. Chloride in sea water⁵ and in organic compounds⁶ was determined similarly by measuring a CuCl band in the region of 437 $m\mu$. In this case a low fuel pressure was used to prevent excitation of oxide bands which are formed in the same spectral region. The range of chloride determined was approximately 0.2 to 1.5 per cent in water and of the same order in organic compounds. For the determination of fluoride, CaF bands which extend from 514.5 to 529 $m\mu$ have been utilized.^{2, 7, 8, 9, 10} The variation in intensity of the bands was observed to be dependent on the fluoride concentration. Fuwa⁸ also observed a similar relationship for SrF and BaF bands at 495 and 500 $m\mu$, respectively. Ishida⁹ studied the effect of temperature and different fuels (propane, H_2 , acetylene) on the intensity of the CaF bands. He detected the CaF bands only with an oxygen-acetylene flame, and found the intensity to be maximum at 2400° K, that is, at a relatively low temperature. In regions of higher temperature it may be presumed the CaF is dissociated.

This technique, the measurement of molecular bands, can probably be extended to the determination of other nonmetallic ele-

ments. Gaydon and Egerton¹¹ present data on some of the bands systems which may be of interest. Among the more prominent bands tabulated are: BrO at 427.0, 439.8, and 453 m μ ; CS at 257.5 m μ ; IO at 458.3 m μ ; SO at 316.5 and 327 m μ ; and SiO at 248.7 m μ .

Indirect methods involving separation of the component to be determined by classical chemical precipitations have been found to be readily applicable in a number of cases. A precipitant which contains an element readily estimated by flame photometry is utilized. Either the excess reagent or the precipitate which contains the desired component in a known stoichiometric ratio is aspirated into the flame and, by referring the measured radiant intensity to a calibration curve, the amount of the desired component is determined. The limitations of this procedure are essentially those associated with gravimetric determinations, and include solubility effects and coprecipitation errors.

One of the earliest applications of this type was the determination of halides.¹² Silver nitrate was added in excess, the residual silver was determined flame photometrically, and the halide concentration was calculated from the decrease in emissivity. Within the range of 30 to 100 μ g of Cl per ml, the coefficient of variation was 5 per cent.¹² Even lower concentrations of chloride (1 to 10 μ g per ml) can be determined. Furthermore, by the addition of ammonia in controlled concentrations to selectively complex halides, individual halies can be determined in the presence of others, for example, bromide in the presence of chloride and iodide in the presence of both bromide and chloride.¹³ Similarly, sulfate can be determined by the addition of a barium salt in excess and subsequent flame photometric measurement of the excess barium,¹⁴ or of a suspension of the barium sulfate precipitate in a 1-per cent starch solution.¹⁵ The ranges of sulfate concentration thus determined were reported to be from 0 to 100 ppm and 100 to 1000 ppm,

respectively. Earlier yet Lundegardh¹² determined sulfate by precipitating it in an ethanol medium with strontium, added in excess, and measuring the excess strontium flame photometrically. He used 25 ml of 0.0015 to 0.005 *M* sulfate solutions. In previous work, Lundegardh¹⁶ also indicated that barium had been used in the determination of sulfate and that a similar technique, utilizing calcium as the precipitant, had been used for the estimation of carbonate by indirect flame photometry. No details were given, however. In a like manner, fluoride was determined by precipitating it as CaF₂, followed by a flame photometric measurement of excess calcium.¹⁷ Here, again, details are lacking.

The precipitation method followed by the application of flame photometry to measure the excess of precipitant can, it is evident, be utilized for the determination of many components for which gravimetric methods are available. Required conditions are: the precipitation must remove the desired component quantitatively and in a fixed and known stoichiometric ratio with the precipitant; the precipitating reagent must contain an element which can be determined by direct flame photometry. This type of analysis should be of particular value for service analysis of a large number of similar samples, the approximate concentration of which is known, especially where results are required in the minimum of time rather than with extreme precision.

In this category may also be included methods for the determination of pure compounds in solutions or mixtures by flame photometric measurement of a constituent of the compound. In this manner Knight and Peterson¹⁸ established the concentration of sodium salts of organic acids by measuring the emissivity of the sodium. This technique has also been utilized for the determination of CN and NO₂ present as their potassium salts.⁴

Cation displacement on an ion exchange

resin column followed by measurement of the emissivity of the displaced cation can, under suitable conditions, be utilized for determination of the adsorbed ion. For example, magnesium, an element which yields, at best, a feeble flame spectrum, has been determined by measurement of the emissivity of sodium equivalent to the magnesium, which was displaced from a cation exchange column.³

In the third grouping, the determination of a component is based on the magnitude of its interference with the emissivity of another component, for example, through compound formation.¹⁹ This type of effect has been applied as an indirect method for the determination of phosphate²⁰ and aluminum,²¹ through measurement of the extent to which they inhibit the emissivity of calcium, under controlled operating conditions. Similar techniques have been reported by others.²² Procedures based on interference effects have been proposed for the determination of sulfate, molybdate, tungstate, vanadate, arsenate and zirconate.³ Of the indirect flame photometric methods cited, those based on the application of "interference effects," are probably the least reliable. They are highly empirical and dependent on a thorough knowledge of the matrix material. Many variables such as flame temperature, aspiration rate, side reactions must be accurately controlled or taken into account. Our knowledge of the chemical reactions related to "interference effects" is far from complete. It has been postulated that the emission of calcium is depressed by the formation of compounds which are difficult to decompose¹⁹ or dissociate,²³ and similar effects have been reported for other alkali earth elements and also for elements of the alkali group. Perchloric acid has been observed to enhance the interference attributable to phosphate.²⁴

Through the use of indirect methods the applicability of flame photometry can be extended to the determination of a substantial

number of elements for which direct methods are not available. In the application of these techniques, however, one must recognize and allow for the restrictions and limitations imposed and the non-specific nature of some of the procedures.

Currently, Dean in his book presents some additional information on this subject.²⁵

REFERENCES

1. HERRMANN, ROLAND, "Flammenphotometrie," Springer-Verlag, Berlin, 1956, p. 181.
2. BURRTEL-MARTÍ, F., AND RAMÍREZ-MUÑOZ, J., "Flame Photometry," Elsevier Publishing Co., Amsterdam, 1957.
3. GILBERT, PAUL T., JR., "Analytical Flame Photometry: New Developments," Paper No. 227, Third Pacific Area National Meeting of the American Society for Testing Materials, San Francisco, California, October 11-16, 1959, p. 29-31.
4. HONMA, MINORU, AND SMITH, C. LONTHROP, "Quantitative Analysis of Organic Nitrogen by Flame Spectroscopy," *Anal. Chem.*, **26**, 458 (1954).
5. HONMA, MINORU, "Flame Photometric Determination of Chloride in Sea Water," *Anal. Chem.*, **27**, 1657 (1955).
6. MARSH, GRACE E., "A Routine Flame-Photometric Determination of Organic Chloride," *Applied Spectroscopy*, **12**, 113 (1958).
7. FUWA, K., "Spectrochemical Analysis of Fluorine by Band Spectrum of CaF," *J. Chem. Soc. Japan, Pure Chem. Sect.* **75**, 1257 (1954).
8. FUWA, K., *Ibid.*, **76**, 14 (1955).
9. ISHIDA, *Ibid.*, **77**, 241 (1956).
10. MITCHELL, R. L., "The Spectrographic Analysis of Soils, Plants, and Related Materials," Commonwealth Bureau of Soil Science, Tech. Commun. 44, Harpenden, England, 1948.
11. GAYDON, A. G., AND EGERTON, ALFRED, "Spectroscopy and Combustion Theory," 2nd Ed. Revised, Chapman and Hall Ltd., London, 1948. M
12. LUNDEGARDH, HERRIK, "Die Quantitative Spektralanalyse der Elementer," p. 66, Gustav Fischer, Jena, 1934.
13. MENIS, OSCAR, HOUSE, H. P., AND RAINS, T. C., "Indirect Flame Photometric Method for Determination of Halides," *Anal. Chem.*, **29**, 76 (1957).
14. BURRTEL-MARTÍ, F., RAMÍREZ-MUÑOZ, J., AND REXACH-M DE LIZARDUY, M. L. "Indirect

FLAME PHOTOMETRY

- flame-photometric determination of sulfate ions," *Anal. chim. Acta*, **17**, 559 (1957).
15. CULLUM, J. C., AND THOMAS, D. B., "The Determination of Barium and Sulfate with E. L. Flame Photometer," *Analyst*, **84**, 113 (1959).
 16. LUNDEGARDE, HERRIK, "Die Quantitative Spektralanalyse der Elementer," Gustav Fischer, Jena, p. 143, 1929.
 17. Beckman Application Data Sheet, DK-92-C, "Indirect Flame Method Simplifies Fluoride Measurements in Cleaning Bath Solutions," no date.
 18. KNIGHT, SAMUEL B., AND PETERSON, M. H., "Flame Photometric Determination of Sodium in Salts of Organic Acids," *Anal. Chem.*, **24**, 1514 (1952).
 19. MARGOSHES, MARVIN AND VALLEE, BERT L., "Instrumentation and Principles of Flame Spectrometry. Effect of Extraneous Ion in Simultaneous Determination of Five Elements," *Anal. Chem.*, **28**, 180 (1956).
 20. DIPP, WILLIAM A., BRICKER, CLARK E., AND FURMAN, N. HOWELL, "Flame Photometric Determination of Phosphate," *Anal. Chem.*, **26**, 553 (1954).
 21. CENCELJ, J., "Die Indirecte Flammenphotometrische Aluminum-Bestimmung," Proceedings of the Colloquium Spectroscopicum Internationale VI, p. 62. Amsterdam, May, 1956.
 22. MITCHELL, R. L., AND ROBERTSON, I. M. "The Effect of Aluminum on the Flame Spectra of the Alkali Earths. A Method for the Determination of Aluminum," *J. Soc. Chem. Ind.*, **55**, 269 T (1936).
 23. MARVODINEANU, R., AND BOITEUX, H., *L'Analyse Spectrale Quantitative par la Flamme*, Masson et Cie, Paris, 1954, p. 85.
 24. BAKER, GRAEME L., AND JOHNSON, LEON H., "Effects of Anions on Calcium Flame Emission in Flame Photometry," *Anal. Chem.*, **26**, 465 (1954).
 25. DEAN, JOHN A., "Flame Photometry," p. 261, McGraw-Hill Book Co. Inc., New York, 1960.

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LESS FAMILIAR ELEMENTS

Of all the flame photometers in use throughout the world (there must be at least 10,000), a great majority are doubtless employed for the determination of sodium and potassium. Every one now knows that these

elements, troublesome to determine by chemical means, yet of great importance in many fields, yield most easily to flame analysis. Protagonists of flame photometry can have no quarrel with this state of affairs. But there are many who believe that the flame ought to be much more widely advertised as an emission source for the 60 or so other elements amenable to determination by flame spectrophotometry.

Valuable service in this direction is being rendered by Dean's book,¹ which appeared in July, 1960; much of it is devoted to a critical discussion of the flame emission characteristics of the elements. The book by Herrmann and Alkemade,² scheduled to appear in August, 1960, covers thoroughly the entire subject and contains detailed tables of wavelengths and some 70 recordings of the flame spectra of the elements. A translation of Herrmann's first edition,³ to appear shortly, contains the same material on flame spectra. A recent review⁴ presents many new spectrograms, condensed tables of flame spectra, and 340 references emphasizing various recent highlights and the rarer elements.

Atomic absorption spectroscopy (absorption flame photometry) is an allied technique which is being rapidly exploited at present. It is applicable to some of the elements less commonly determined by flame (Al, Cd, Co, Au, Pd, Pt, Rh, Ag, Tl, Sn, Zn). For reviews see reference 4 and especially reference 5; also "Atomic Absorption Spectrochemical Analysis" (Malmstadt), p. 12.

Regarding their determinability by emission flame spectrophotometry, the chemical elements fall into seven groups:

(1) *Elements rather commonly determined:* Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Cr, Mn, Fe, Cu, B. The boundary between this and the next group is vague; Rb and Cs might be relegated to group (2), while Co, Ni, Ag, Tl, and Pb might be included in (1).

(2) *Elements easily determined but more or less neglected:* Ra, Sc, Y, La, Pr, Nd, Pm,

Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ti, V, Co, Ni, Ru, Rh, Pd, Ag, Cd, Al, Ga, In, Tl, Sn, Pb, P, Sb, Bi. These have a characteristic spectrum with detection limit of 1 ppm or better with a commercial flame spectrophotometer. A few elements with good spectra (Ge, As, Te) are in the 2-5 ppm range.

(3) *Elements with distinctive but less sensitive flame spectra:* Be, Mo, Re, Pt, Au, Zn, Hg, Ge, N, As, Te. (Detection limits 2 ppm or over.)

(4) *Elements emitting only a continuum with or without weak bands:* Ce, Th, U, Zr, Nb, Os, Ir, I. The continuum may, however, be quite intense.

(5) *Elements of unknown flame spectrum:* Ac, Pa, Np, Pu, Hf, Ta, W, Tc, Si, Se, Po. (Si and Se have been studied, but their analytical determinability is unknown.)

(6) *Elements too rare for flame analysis:* Fr, At, and the trans-plutonium elements Am through No. (But Am and Cm may now be sufficiently available to permit flame analysis.)

(7) *Elements not amenable to direct flame analysis:* H, C, O, S, F, Cl, Br, and the noble gases. (But F, Cl, and Br can be determined by their metallic halide spectra, while C is determinable in a hydrogen flame and certain S compounds have characteristic flame spectra.)

As for group (1), there are a thousand publications concerning flame-photometric determinations of sodium and potassium, hundreds on calcium, lithium, magnesium, and strontium, and dozens on each of the rest. Even for rubidium there are about 90 publications discussing its flame determination. Although an element such as magnesium is far from being "usually" determined by the flame, it can be handled so expeditiously by the best commercial flame spectrophotometers, and there is such extensive literature in this domain, that it must be ranked as one of the elements commonly determined by flame photometry.

Our concern here is with the much larger number of elements having strong and distinctive flame spectra which, nevertheless, are seldom or never determined by flame photometry. Ruthenium is a good example. Its flame spectrum comprises a very characteristic group of lines. With the best commercial instruments its limit of detection is about equal to that of rubidium, below 0.1 ppm. Flame spectrograms are available in Lundegårdh's classic work (1929 and 1934), in the excellent monograph by Mavrodineanu and Boiteux,⁶ and in Dean's book.¹ Yet there appears to be no record of any one having used the flame for the analytical determination of ruthenium. This seems the more singular in view of the difficulties besetting the analysis of the platinum metals.

Although flame photometry normally consumes the entire sample, the method can be kept economical enough to warrant its use for scarce materials. Several atomic energy establishments are determining fission products by flame photometry. There are a dozen reports on the flame analysis of uranium for impurities (Li, Na, K, Mg, Ca, Ga, In, Tl, Fe). A special instrument was built at Oak Ridge National Laboratory⁷ for the determination of cesium down to the parts-per-billion range. To be sure, the combustion products must be filtered to prevent dissemination of radioactivity.⁸ A flame spectrophotometer has been rigged for remote-control operation inside a "hot cell."⁹ Among the rarer elements listed above, it is likely that at least actinium, technetium and americium will reveal such sensitive and distinctive flame spectra as to permit their determination at low concentrations. Some of the elements of group (6) are, however, hopelessly rare: no information yet exists on the optical spectrum of francium, for example.

The assignment of the elements to the various groups above depends intimately on the analytical conditions: choice of flame and solvent (i.e., the chemical environment) and the instrumentation. Table 1 lists the

FLAME PHOTOMETRY

principal emissions of the elements in four different flames, and in water or various favorable organic solvents, as observed with a widely used make of flame spectrophotometer.

Burner and Atomizer

The air-hydrogen, oxyhydrogen, and oxyacetylene flames listed in Table 1 are generated by an atomizer-burner¹⁰ that yields a high luminous efficiency; some of its characteristics were described recently.¹¹ A similar atomizer-burner has been developed in Germany.¹² Another type of atomizer-burner¹³ produces a larger flame offering better sensitivity for some elements; a similar type¹⁴ is utilized by Warren¹⁵ in a flame spectrophotometer which appears to be the most sensitive general-purpose instrument yet built. This high sensitivity is achieved through a combination of burner design and high dispersion and luminosity of the large prism monochromator. An intermediate type of atomizer-burner, operating on oxygen and gas, is employed in a popular make of filter photometer.¹⁶ Except for this last, most simple instruments intended for routine work (sodium, potassium, and sometimes calcium) use the older types of burner with separate atomizer: atomizer-burners are almost universally used for the more difficult elements. The oxycyanogen flame listed in Table 1 was generated with a premixing burner having a separate atomizer,¹⁷ but considerable work with oxycyanogen has been done with a premixing atomizer-burner.¹⁸ A similar premixing atomizer-burner, burning oxygen-propane, is utilized in an interesting automatic flame photometer recently placed on the market.¹⁹ It may be stated that current developments in burner design will result in simple atomizer-burners that can handle almost any combination of fuel and oxidant while providing greater stability and emission intensity than have been hitherto available with such devices.²⁰

Closely associated with the nature of the

flame and burner is the matter of sample pumping. With small samples or scarce materials and for optimal excitation of difficult elements, control of sample flow may be very critical, especially with oxycyanogen. Methods of obtaining readings from atomizer-burners with samples less than 0.1 ml, which pass through the flame very quickly, are described by Warren¹⁵ and by Exley.²¹ The subject of sample flow control is reviewed by Gilbert.⁴ See especially the papers by Baker *et al.*^{22, 23}

Solvent

The solvent, of course, constitutes part of the flame and may contribute much or conceivably all of the fuel. Also, its atomizing characteristics and the heterogeneous situation prevailing near the evaporating droplets affect the nature and intensity of the emitted spectrum. It is obvious from the Table that the choice of solvent may be all-important in certain analytical applications. This is a large subject with an extensive literature; for an up-to-date introduction, see the able review by Dean.¹ The application of liquid-liquid extraction to flame photometry (often with the help of chelating agents), pioneered by Dean and his collaborators, has been especially fruitful. A particularly interesting effect utilized in producing line spectra of the rare earths was described by Fassel²⁴: when an alcoholic solution of a rare-earth perchlorate is sprayed into an oxyacetylene flame, the additional energy liberated by oxidation of the carbon-hydrogen compounds by the perchlorate in the immediate vicinity of the evaporating droplets is sufficient to dissociate many of the rare earth oxides and to excite the resulting metal vapors, yielding rich and useful spectra of the elements. The effect was reported for Sc, Y, Sm, Eu, Dy, Ho, Er, Tm, Yb, and Lu, but quantitative data are not yet available.

A somewhat similar effect, apparently a true chemiluminescence, earlier noted by Lundegårdh, Mandel'shtam, Mavrodineanu,⁶

Gaydon, and others, and elucidated by J. C. Sternberg, was reported by Gilbert.²⁵ It occurs in the air-hydrogen flame with an alcoholic solvent (or any other organic material in the flame). Elements that form gaseous monoxides in the flame are reduced to metallic vapor presumably by free atomic carbon formed in the reaction zone: $MO + C = M + CO$. Since CO has the very high dissociation energy of 11.1 eV, the metal atom M may come away with a greatly superthermal excitation. Thus, GeO, with a dissociation energy of 5.5 eV, can yield Ge atoms with over 5 eV of excitation, sufficing to develop the full arc spectrum of Ge in this comparatively cool flame. In the case of tin, the low dissociation energy of SnO (3.2 eV) permits the Sn to be ionized (ionization potential 7.3 eV); both arc and spark spectra of tin appear. As seen in Table 1, Ge, Sn, Pb, As, Sb, Bi, and Te show this chemiluminescence useful. Some of these elements would not otherwise be readily amenable to flame analysis. The excitation does not occur with P, for the dissociation energy of PO (6.2 eV) and the excitation energy of its ultraviolet lines (7.1 eV) add up to more than 11 eV. However, the PO band spectrum is strongly emitted in the air-hydrogen-alcohol flame. Many elements remain to be studied in this source.

Spectrophotometry

The data in Table 1, although representing the capabilities of a particular American make of flame spectrophotometer, would be almost equally valid for the flame spectrophotometers with atomizer-burners that are now manufactured in England, Germany, and Japan. There are indications that instruments appreciably superior to those now made will before long appear on the market. The improvements will necessarily apply to the three factors that chiefly control the sensitivity of an emission spectrophotometer: the quantum efficiency/dark current ratio of the photocathode, the dispersion,

and the light-gathering power (luminosity) of the monochromator. The long-term stability of the source (limiting the time constant that can profitably be applied) enters in too. The relationships existing between the figure of merit (measure of sensitivity) of an emission spectrophotometer and the factors controlling it have not yet been fully expounded in any published work; but see Herrmann.² As a rough generalization, the sensitivity as measured by the detection limit of an element in the flame improves about as rapidly as the square root of the product of photocathode sensitivity, dispersion, luminosity, and source stability. Therefore significant improvement in flame spectrophotometers is likely to entail a decided increase in cost.

One area in which immediate improvement can be realized is in the red end of the spectrum. The RCA 1P28 photomultiplier, used over the range 200 to 650 or 700 $m\mu$ in most studies of the flame spectra of the less familiar elements, already enjoys such high quantum efficiency (and low dark current) up to about 600 $m\mu$ that its performance is not far from the limit imposed by the corpuscular nature of light. But beyond 600 and especially beyond 700 $m\mu$ there is much room for improvement. Within the last year or two an impressive assortment of red-sensitive photomultipliers has appeared on the market. The topic is reviewed in reference 4, but several new photomultiplier tubes have appeared.

Intensity and Detection Limit

Of the many ways in which spectral intensities can be and have been expressed, the one chosen for Table 1 is believed to be especially practical for flame photometry, even though an emission cannot be fully described with a single number. The intensities are computed for the Beckman DU spectrophotometer with flame and photomultiplier attachments; the intensity $J = 100 (R - B)/B$, where B is the blank reading (pure

TABLE 1. FLAME SPECTRA OF THE ELEMENTS: CONDENSED TABLE OF PRINCIPAL FEATURES
(See text for description of instrument and definition of intensity.)

Legend: AH air-hydrogen, OH oxyhydrogen, OA oxyacetylene, OC oxycyanogen; solvent is water. AHn, OHn, OAn, the corresponding flames with nonaqueous solvent; the solvent is indicated, for each group of data, by the following symbols: AA acetylacetone, Ac acetone, Bu butanol, Bz benzene, C chloroform, EA 1:2:1 ether-alcohol-water, G gasoline, H hexone, K kerosene, M methanol, N naphtha, P isopropanol; subscript number indicates percentage, e.g., Ac₅₀ = 50% acetone + 40% water. Other notations: () very doubtful; a are line, b band peak, c continuum or very wide band, d double, f intercombination line, i inner cone emission, k with an 8-1 photomultiplier, m multiple, p resonance line, r head of red-degraded band, s spark line, t triple, u unclassified line, v head of violet-degraded band, w wide or diffuse band, x with uncoated mirror in burner housing (mirror normally has a silicone coating).

Notes: (1) Seen in absorption against an effectively hotter OH band. (2) Data to be provided by Kniseley, Fassel and Curry, *Spectrochimica Acta*. (3) Obscured by CN bands. (4) Bands emitted only from iodate solution. (5) For 1P28 photomultiplier with red filter. (6) The are lines 382.04, 383.23, 383.83 sometimes appear within this band. (7) The stronger bands 386-388 are interfered with by CH 387, 389.

Species	Character	Wave-length	Intensity in various flames						
			AH	AHn	OH	OHn	OA	OAn	OC
Ag	p	328.07	100		100	100 EA	50	30 EA	25
	p	338.20	250		170	170	50	40	20
Al	p	394.40	pc 0.3		0.8	20 H	1	100 H	25
	p	396.15	pc 0.35		1.0	30	2	200	30
AlO	r	467.2	rc 0.8		2	10	0.15	17	0.0
	r	484.2	1.5		3	50	0.3	70	0.0
	r	510.2	rc 1		2	10	0.2	17	0.0
As	a	228.81 x		2.5 P			(0.1) i		0.1
	a	234.98 x	0.1	4	1		1.1		0.03
Au	p	242.80 x	0.3		2		1.7		
	p	267.60 x	5		30	50 Bu ₄	5	8 M ₅₀	0.0
BO ₂	db	494	8		50	80	6	15	0.0
	b	518.0	11		60	90	15	17	0.0
	b	547.6			30	70	10	10	0.0
Ba	p	579	7		40	100 Bu ₄	50	50 N	5
Ba ⁺	s	553.56	170		8	20	10	100	100
	s	455.40	c 8		25	40	50	100	70
BaOH	sb	493.41	c 80		30	40	50	5	0
	b	488	100		30	50	70	5	0
	b	513	150		30	50	5	(300)	0
	b	880	200 k		30	25 Bz	5	(300)	0
	b	873	80 k		30	25	0.0		0
Be	p	234.86 x	0.0		0.0		0.0		0
BeO	r	470.9			0.7		0.25		0
	r	473.3	rc 0.2		0.5		0.2		10

Bi	dp	223.0 x	7 P	0.017	0.005 P	0.01 i ¹		0.0
	p	306.77	0.2	0.25	1700 Bu ₄	250	1000 EA	3
Ca	a	472.26	0.00	1000		0.05		0.0
Ca ⁺	p	422.67		sc 25		sc 30		400
CaOH	s	393.37		1700	2500 Bu ₄	170	700 EA	500
	b	554		700	1000	250	300	10
	b	602		2500	5000	500	1000	3
Cd	p	622	20 P	1	17 P ₆₀	0.25		10
	f	228.80 x	6	2	5 Ac	0.25	5 Ac	20
CeO	bc	326.11		7	5 Ac	0.7		0.4
(Ce)	c	494		10	10	0.7		
Co	a	550-600		20	30 Bu ₄	5		9
	dpf	340.51		25	30	3		9
	dap	341.25		25	50	7		50
	a	345.4		25	30	3		7
	tap	350.23		17	50	7		10
	da	352.8		35	30	4		*
Cr	a	357.35	15 P _{as}	20	30 N	20	1000 H	50
	p	357.87	15	80	150 Ac _{ss}	20	900	120
	p	425.43	8	100	110	17	550	110
	p	427.48		80	80	12	300	80
	ta	428.97		70	70 Bu ₄	10	100	80
CrO	re	520.6		20	120 Bu ₄	15		0
Ca	a	579.4		25	30 Bu ₄	0.3		0.03
	p	455.54		1000	2000	1000		40
	p	852.11 k		300	700	300		10
Cu	p	894.35 k		100	500 M	100	300 K	30
	p	324.75	40 P _{as}	100	500	100	300	20
CuOH	w	327.40	25	17	20 Bu ₄	6		0
DyO	w	537		80 H	80 H			
	mr	526.3		70	70			
	b	540.0		60	150			
ErO	b	572.9		120	150			
	b	583.3		120	65 H			
	b	504		30	80			
	b	552		50	35 H			
Eu	p	459.40		25	30			
	p	462.72		20	120 H			
(EuOH)	bc	598		100	100			
	wc	623		70	150			
	wc	647		25	100			
	w	702		50				

TABLE 1.—Continued

Species	Character	Wave-length	Intensity in various flames						
			AH	AHn	OH	OHn	OA	OAn	OC
Fe	a	302.06	4	5 P ₃₅	2.5	50 H	1.5		50
	p	371.99	80	11	40	50 Bu ₄	15	100 AA	20
	(d)p	373.71	80	10	30	50	8	70	14
	tp	374.7	70	8	25	50	6	50	11
FeO	(d)p	385.99	70	9	35	50	11	70	3
	re	564.7	c 170		40	120 Bu ₄	10	3 M ₂₀	0
	re	581.9	c 170		40	120	11	3	0
	p	403.30	10		100	150 Bu ₄	10		0
Ga	p	417.21	20		200	300	20		
	r	461.6			17	30 H			
	mr	580.7	(5)		50	120	(10)		
	mr	598.7	(10)		80	250	(20)		
Ge	bc	623	(10)		70	250	(20)		
	u	259.25 x		0.7 P	0.01	0.025 P ₃₀	0.015 i	0.025 i P ₃₀	
	dp	265.14 x	0.00	2		0.03	0.04 i	0.05 i	
	f	253.65 x	1.7	2.5 P	0.3	1.7 Ac	{0.2 1.2 i		
Hg	r	515.7			50	50 H			
	b	527			50	50			
	b	532.0			50	50			
	b	565.9			120	170			
IO	re	494.5			(1) ⁴				0.00
	re	513.1			(1)				0.00
	re	530.8			(1)				0.00
	re	410.18			200	300 Bu ₄	50		
In	p	451.13	150	50 P ₃₅	350	500	70		
	p	404.5	250	80	70	100 Bu ₄	10		
	da	766.49 k	30	1 P ₃₅					
	p	769.90 k	10,000		30,000	50,000	{30,000 20,000		0.15
LaO	p	438.0	5		25	25 H	17	80 H	}300
	mr	442.3	5		25	30	17	80	
	mr	560.0	17		70	100	17	170	
	r	743 k	30		20	1000	100	120	
Li	mr	792 k	25		20	1000	100	150	
	mr	610.36	30		20	30 Bu ₄	10		
	a	670.78 ^s		1500 P ₃₅	50,000	70,000	10,000		25
	p	486.2	10,000			80 H			3000
LuO	mr	517.0		20 P ₃₅	30	110			
	mr	285.21	100		100	250 Ac	70		
	p							100 EA	1000
	p								

MgOH	b	370.2	500	60	100	100 EA	5		0
Mn	mb*	381-383	500	50	80	80	3.5		0
MnO	tp	403.2	500		1000	1500 N	500		120
	r	538.9	100		50	80 Bu ₄	8		0.2
	r	558.6	120		80	120	17		0.15
Mo	p	379.83	c 2.5	0.0 P ₈₀	c 0.8	10 i N	(0.5) i	20	3
	p	386.41	c 3	0.0	c 0.8	10 i	(0.3) i	20	1*
(MoO ₃)	p	390.30	c 3	0.0	c 0.8	5 i	(0.25) i	20	11
NC	c	550-600	25		10	0.17 iN	(3)	20	0
NO	dv	385.37							
	dv	226.3 x		0.4 P					
	dv	236.3 x		0.5					
Na	da	330.3	2.5		20	10 Bu ₄	10		0.5
	dp	589.2	30,000		50,000	70,000	25,000		2000
	da	819 k			5	10	20		10
(Nb)	c	550	5		1		0.3		
NdO	mb	660			10	100 H	10		
	bc	691			10	500	5		
	bc	702 k			10	500	10		
	tbs	712 k			10	500	10		
Ni	p	341.48	80	25 P _{as}	50	60 Bu ₄	10		50
	dp	346.0	45	15	30	30	7		20
	p	349.30	25	10	20	25	7		20
	p	351.51	45	15	22	30	9		20
	p	352.45	80	25	50	80	15	(50) C	30
	a	361.94	40	10	22	30	5		20
PO	vb	238.3 x	0.4	8 P					
	v	246.4 x	0.5	10					
(P)	c	520	30		5	7 G	0.1	5 G	2.5
Pb	a	303.96	1.5	2 G	10	15	0.2	10	7
	a	368.35	3	4	10	15	0.3	10	7
	a	405.78	3	4	70	200 H	10		80
Pd	a	340.46	45		45	90	7		50
	a	360.95	30		80	150	10		100
	a	363.47	55		(10)	(50) H	(1)		
(PmO)	b	(640)			(10)	(50)	(1)		
	b	(680)			15	11 H	(1)		
PrO	rc	576.3			10	20			
	dr	603			10	50			
	bc	709.5 k			(10)	30			
	dre	735 k			(10)				

TABLE 1.—Continued

Species	Character	Wave-length	Intensity in various flames						
			AH	AHn	OH	OHn	OA	OAn	OC
Pt	p	265.95 x	0.11		0.8				8
Ra	p	306.47	0.25		1		0.5		7
Ra ⁺ (RaOH)	p	482.59			(5)				
	s	381.44			(3)				
	b	627			(5)				
	b	665			(5)				
Rb	a	420.19	20		35	50 Bu ₄	2		0.1
	p	780.02 k	3500		3500	5000	2000		100
Re	p	794.76 k	2500		2500	3000	1700		50
	p	488.92			(0.1)				
	p	527.55			(0.1)				
Rh	p	339.68	pc 4		8	12 P	5	8 P	
	p	243.49	2.5		15	25	9	17	
	p	350.25	pc 3.5		8	10	5	8	
	a	365.80	ac 6		11	15	6	9	
	p	369.24	7		35	40	15	22	
	a	370.09	ac 6		11	11	4.5	8	
Ru	p	349.89			5	30 M ₅₀	3		
	p	372.80			20	150	30		
	p	379.9			10	100	25		
Sb	tp	217.59 x	17 P						0.2
	p	231.15 x	25						
	a	262.85 x	8				(0.1) i		
	a	259.81 x	0.01				(0.1) i		
SeO	r	485.8	0.025						
	r	581.2			20	60 H	5		
	r	607.3			40	150			
	tr	611.0			250	1700	30		
SiO	tr	241.4 x		0.00 P ₅₀	200	1200	25		
	r	248.7 x		0.00		(0.1)			
	r	256.4 x		0.00		(0.1)			
SmO	mbe	614				80 H			
	mbe	624			40	80	2		
	tbe	642			30	100	2.5		
	mbe	652			20	110	3		
Sn	a	235.48 x	15 P			1.5 iP			
	a	242.95 x	15			1.5 i			
	a	270.65 x	12		0.012		1.7 i		8
	a	284.00	11		(0.015)		0.2 i		10
	p	303.41	12		0.05		{0.05 0.4 i		

SnO	r	358.5	3	0.5 P ₂₅	0.9	0.22 Ac ₈₀	0.2		
Sr	p	460.73	500	150 P ₂₅	1000	2000 Ac ₈₀	200		150
Sr ⁺	s	407.77			30	50 Bu ₄	17		400
SrOH	b	605	5000	250 P ₂₅	1000	1500 Bu ₄	100		
	b	666	500		700	1000	40		
	b	680	250		1000	1000	30		
TbO	b	534			40	60 H			
	bc	573			50	100			
	bc	592.1			80	170	(10)		
	bc	598.0			70	150	(10)		
Te	da	238.5 x	0.01	1 P	0.3		0.000		
TeO	dre	371.4	3.5		0.2		c 0.015		
	dre	377.3	3.5		0.25		c 0.015		
	tre	382.7	3.5		0.25		c 0.017		
	tre	388.4	3.5		40		c 0.017		
TiO	re	516.7			45		1.5 P		
	re	544.9			45		1.5		
	re	575.9			45		1.5		
	bc	715			20				
Tl	p	377.57	50		100	170 Bu ₄	10		6
	a	535.05	30		70	100	10		8
TmO	b	491			30	50 H	5		
	b	538			35	60			
	b	541.5			35	60			
(UO ₂)	c	550	15		5				
V	ta	318.4		0.00 P ₅₀	30	80 Bu ₄	5		23
VO	re	522.9	80	c 17 P ₅₀	40	100	7		0.0
	re	547.0	100	c 17	40	110	10		0.0
	re	573.7	110	c 30	30	50 H			0.0
YO	r	481.8			300	1000			
	mr	599			300	800	30		
	mr	615			300	120 H	30		
Yb	a	398.80	70		25		(10)		
	pb	555.65	250		70	60	(10)		
(YbOH)	b	498.1	200		50	50 H	(5)		
	b	532.5	250		80	80	(5)		
	b	572.5	300		110	100	(10)		
Zn	p	213.86 x	0.04	0.15 P ₅₀	0.06	1 Ac	0.017		6
	a	481.05	c 0.3		c 0.06	0.6 iN	i	c 6 Ac	0
(Zn)	c	520-600	0.5		1.2	12 Ac	(0.1)	4	0
ZrO	bc	564			1.2		(0.1)		0
	bc	574			1.2				0

solvent) and R is the reading for a solution containing 10 mg of the element per liter for the slit width at which, for the blank, shot-effect noise equals flame flicker. Beyond 700 $m\mu$ intensities are computed for a Farnsworth 16PMI photomultiplier. Between 620 and 700 $m\mu$ the usual 1P28 photomultiplier will give the intensities listed, but the 16PMI will permit narrower slits. The slit width implied in this definition ranges from 0.01 mm for oxycyanogen and some regions of the oxyacetylene spectrum to 0.5 mm or more for air-hydrogen; it varies inversely as the square root of the absolute blank intensity.

The quantity $10/J$ then gives the detection limit, defined as the minimal concentration of element in mg/liter (in a solution containing no interfering materials) yielding a net signal equal to total peak-to-peak noise for a time constant of 1 second. Beyond 700 $m\mu$, for the red-sensitive phototube of the DU (where shot noise is not the limiting factor), the detection limit for lines is about $300/J$ instead of $10/J$; for bands it will vary between these values, depending on wavelength, flame, and width of the band. This type of definition is a realistic one for lines and sharp bands, and is favored by Alkemade, who, in his thesis,²⁶ gives a very careful analysis of the fundamentals of flame photometry. It is a fortunate fact that in working with line spectra at concentrations close to the detection limit, much narrower slits (seldom over 0.05 mm) can often be used than those implied by the definition, without loss of effective sensitivity. (The greater relative noise is compensated by greater line/background ratio.)

Interferences

This large subject is best covered by Herrmann and Alkemade.³ Dean¹ gives the most extensive tables of inter-element interferences. Both works should be consulted. See also reference 4 for a review of condensed-phase interference and the use of releasing

agents and protective chelating agents for circumventing it. These two methods have rapidly increased in use in 1960. Likewise, self-standardization (standard addition) is becoming popular as a means of avoiding many kinds of interference in flame photometry; Teloh's book²⁷ gives practical methods. To define these terms briefly: Interference, roughly, includes any effect which alters the emission or disturbs the determination of an element. In condensed-phase interference a compound of the element sought, crystallizing out of the evaporating droplets, is not fully vaporized on passing through the flame; one of the most familiar instances is the quenching of calcium emission by phosphate, owing to the low volatility of calcium phosphate. A releasing agent preferentially combines with the interferent, leaving the element sought free to vaporize in the flame; thus, lanthanum releases calcium from phosphate interference. In protective chelation, the element sought is complexed to prevent it from combining with the interferent; e.g., EDTA, by chelating the calcium, prevents the formation of calcium phosphate crystals in the flame, although, of course, the chelate is promptly decomposed by the heat. In self-standardization, a known concentration of the element sought is added to the unknown sample, and the emission is measured before and after the addition. Spectral interference, discussed below, results from proximity or superposition of wavelengths of emissions of different elements.

The flame spectra of many of the less familiar elements are complex; in a mixture there may be many cases of spectral overlap. Wavelength tables as given in references 2, 6, 28 indicate possibilities of spectral interference of lines, but with bands it is difficult to anticipate this, owing to their various widths and structures. Here a set of spectrograms will be very helpful. The best collections are in references 1, 2, 3, 4, 17, 24, 29, 30; note, particularly, the table of spectral

interferences among the rare earths in reference 30. In working with an element close to its detection limit in a mixture, the identity and presence of a chosen line can generally be established by taking readings on and off (but close to) the line; with bands this is less practical unless the band is narrow or has a head. Fortunately many of the bands useful in flame photometry do have heads, being degraded to longer wavelengths, and a reading off the peak can be made just to the violet side of the head. But with diffuse bands like those of ytterbium this technique yields dubious results unless other elements likely to interfere spectrally are known to be absent; if they are not, a concentration perhaps several times the detection limit for pure solutions is needed for positive detection. The same is true if the bands of the element protrude only moderately above its continuum, as with vanadium in the cooler flames. A purely continuous emission, as of Nb, Mo, or U, can permit accurate (and sensitive) flame-photometric determination only when the sample composition is under rigid control, so that the difference between the sample and blank readings can be ascribed unequivocally to the element sought.

Indirect Methods

There are three general kinds of indirect determination: (1) The element sought forms an emitting molecule with a deliberately added material. (2) The element sought does not emit, but exercises a measurable interference on a deliberately added, emitting element. (3) The element sought is precipitated by an excess of an emitting element, which is then determined in the precipitate or the filtrate. These methods are, on the whole, of increasing sensitivity in the order named. For reviews, see Chap. 20 of reference 1 and also reference 4. Examples of the first method include the determination of chlorine by addition of copper and measurement of the CuCl band at $436\text{ m}\mu$ ³¹; of fluorine by addition of an alkaline earth and

the bands $529\text{ m}\mu$ of CaF, $578\text{ m}\mu$ of SrF, or $495\text{ m}\mu$ of BaF; of carbon by the C₂ and CH bands appearing in a hydrogen flame; and of nitrogen by the CN bands appearing in a carbonaceous flame. (These latter two are really direct methods.) The detection limit in these cases is usually above 100 ppm.

Flame-photometric titration belongs to the second method (utilizing interference): for instance, a phosphate solution is titrated with barium, readings being taken on the barium emission; a break-point occurs, corresponding to the point at which barium phosphate is fully formed, yielding the concentration of phosphate. Other examples of the second method include the determination of sulfate, phosphate, molybdate, tungstate, arsenate, vanadate, zirconate, beryllium, and aluminum by their quenching of calcium and strontium³²; and of zirconium via strontium or barium.³³ Examples of the third method are the determination of halides (separately by masking with ammonia) by precipitation with excess silver; of boron by precipitation of barium borotartrate and determination of the excess barium³⁴; of bicarbonate by determining the barium in the precipitated barium carbonate³⁵; of sulfate via excess barium and determination of the barium either in the filtrate¹ or in the precipitate slurried with a starch solution.³⁶

The elements mentioned above can sometimes be better determined by direct methods. Aluminum emits a very good spectrum in organic solvents.¹ Beryllium has a characteristic but (in aqueous solution) not very sensitive band spectrum, while in oxycyanogen its resonance line is strong. Zirconium has a weak band spectrum on a continuum. Phosphorus should be easily determinable by its sharp band spectrum in the deep ultraviolet in air-hydrogen with alcohol. It has also been determined by its continuum in the visible.³⁷ Arsenic has a good line spectrum in the air-hydrogen-alcohol source. Vanadium has a sensitive band spectrum with sharp heads, but the continuum is

strong. Molybdenum emits lines in the inner cone of air-acetylene⁶ and in oxyhydrogen with organic solvents, but the conditions seem very critical. Vanadium and molybdenum emit good spectra in oxycyanogen.⁴ Nothing seems to be known of the flame spectrum of tungsten.

Flame Spectra of the Less Familiar Elements

Some comments on the less commonly determined elements appear below, arranged according to the periodic table.

Beryllium has a band spectrum (due to BeO) rather like that of aluminum; see above. A study of this element in organic solvents might (as proved to be the case with aluminum) be very rewarding.

Radium has a typical alkaline-earth spectrum due to Ra, Ra⁺, and probably RaO and RaOH; it closely resembles that of strontium. However, the wavelength data for the bands are over 50 years old, and there are no modern studies of them, nor any intensity data.

Rare Earths: See especially references 1 and 30; spectrograms of lanthanum, cerium, and ytterbium, along with an up-to-date review, appear in reference 4. Scandium, yttrium, and lanthanum have the most intense spectra, consisting of sharp, closely spaced oxide bands; those of ScO and YO in the orange require high resolution for satisfactory analysis in mixtures. The bands of gadolinium, dysprosium, and lutetium, also due to the monoxides, are sharp and characteristic but less intense. Terbium and holmium have equally strong if rather more complex flame spectra, while those of erbium and thulium are only slightly weaker. Of the lanthanides with quadrivalent tendencies, cerium resembles zirconium in emitting weak bands (of CeO) on a stronger continuum. Praseodymium is similar, but its bands are more prominent and very numerous and complex. Terbium also shows the continuum but its bands are still more pronounced. On

the other hand, europium and ytterbium, tending to bivalence, emit flame spectra much more like those of the alkaline earths: europium resembles strontium, and ytterbium resembles barium. It is suggested that their diffuse bands in the red and green, respectively, are due to EuOH and YbOH. Also the resonance lines of the neutral and ionized atoms Eu, Eu⁺, Yb, Yb⁺ are prominent. Samarium and thulium, less markedly bivalent, also emit (relatively weak) lines. Even dysprosium emits very weak lines in the conventional flames. (Regarding the rich line spectra emitted in oxyacetylene with alcoholic perchlorate solutions, see *Solvent*, p. 348) Neodymium and samarium have complex but distinctive band systems in the red. Promethium has not been studied, but we can guess at the general shape of its spectrum. Despite the severe spectral interferences, Pinta³⁸ has demonstrated the determination of practically all the rare earths in mixtures during separation processes, and there is a modest assortment of recent papers dealing with flame analysis for the rare earths.

Actinides: There is no information on these, except for observations that thorium and uranium emit continua in the usual flames. Their oxides are so stable that higher temperatures would be required for adequate volatilization and excitation. Recall, however, the earlier remarks regarding actinium and americium.

Titanium, Zirconium, Hafnium: Like vanadium, titanium emits bands with sharp heads but superposed on a strong continuum. The zirconium bands are weaker. On zirconium, (see *Indirect Methods*, p. 357). The practical determination of these elements does not seem to have been carried out by flame photometry, although the sensitivity for titanium is good. There appears to be a recent Polish study of the flame emission of titanium.³⁹ Absorption flame photometry is unsuitable, owing to the stability of the oxides. The spark-in-flame method^{4, 40} offers satis-

factory line emission for Ti and Zr. R. Curry of Iowa State University promises a study of Zr and Hf in the usual flames, while J. W. Robinson of Esso Standard Oil Co., Baton Rouge, has observed the oxycyanogen flame spectra of Ti and Zr, but no data are in print.

Vanadium: See above. Vanadate has been determined indirectly by its quenching of calcium⁴¹; but its direct determination in the flame has not been reported, although it seems to have been partly successful in the petroleum industry. Spectra in oxyhydrogen, oxyacetylene, and oxycyanogen are shown in references 1 and 4. The spark-in-flame gives good excitation. The near infrared bands of VO deserve closer study.

Niobium, Tantalum, Molybdenum, Tungsten: See above regarding molybdenum. Niobium emits only a continuum in the usual flames. Tantalum and tungsten probably do likewise, owing to their very low vapor pressures.

Technetium and Rhenium quite possibly have good flame spectra under the proper conditions; they certainly deserve investigation. The observations on rhenium listed in the Table are 30 years old. Lundegårdh found no emission from Re at 2000 ppm in his air-acetylene flame.

Platinum Metals: Like iron, cobalt, and nickel (see references 2 and 3 for spectrograms of these, and reference 1 for discussion), ruthenium, rhodium, and palladium emit sensitive, rather complex line spectra, chiefly in the ultraviolet, admirably suited for flame analysis. However, there seems to be only one reported instance of the use of the flame for a practical determination of any of these elements, *viz.*, palladium.⁴² The application of the flame to Ru, Rh, and Pd is to be strongly urged. Partial spectra for Ru and Pd are shown by Dean,¹ and Gilbert²⁵ has examined Rh in various flames. Photographic spectrograms have been published by Lundegårdh and by Mavrodineanu.⁶ Rh and Pd can be determined by atomic absorp-

tion.⁴ A critical evaluation of the flame spectra shows 30 lines for Ru, about 70 for Rh, and 25 for Pd. The best analytical lines in mixtures of the iron and platinum metals are 379.9 $m\mu$ for Ru, 369.2 $m\mu$ for Rh, and 363.5 $m\mu$ for Pd. Osmium and iridium are stated¹ to emit no flame lines even in organic solvents. These being the least volatile of the platinum metals, it seems likely that the flame would become saturated with vapor at rather low concentrations; yet ruthenium seems capable of attaining a considerable degree of supersaturation. Platinum emits only two relatively weak lines, not yet used for analysis.

Silver and Gold emit only the resonance doublets in hot flames. Gold emits bands in cool flames, coloring the Bunsen flame green, but there seems to be no recent data on wavelengths or emitting species. The intensities listed in the Table for Au (and also for Pt) were derived theoretically. Silver has been repeatedly studied¹ and flame analysis has been resorted to several times. Warren¹⁵ was able to push the detection limit below 0.02 ppm in aqueous solutions with his instrument. Ag and Au are determinable by flame absorption.

Zinc: In common with Mg, Cd, and Hg, zinc emits a resonance intercombination line (at 307.6 $m\mu$), the intensity of which scarcely increases as the flame temperature is raised. Hence these lines are best observed in the air-hydrogen flame with its very weak background emission. Unfortunately the Zn line lies among strong OH bands; otherwise it would be analytically useful. The resonance line proper (213.9 $m\mu$), behaving normally, offers the best sensitivity in oxycyanogen. It is also exceptionally sensitive in absorption.⁴³ The blue line at 481.0 $m\mu$, sometimes appearing in the reaction zone, seems to have been used long ago for practical analysis. However, at present no emission method for Zn can compete with flame absorption.

Cadmium: See reference 1 for a discussion. The intercombination line (326.1 $m\mu$) in air-

hydrogen is best for analysis. Certain visible flame emissions were used for analysis in the past. Cadmium could be determined by absorption, in oxycyanogen, or by spark-in-flame.⁴⁰

Mercury: The intercombination line (253.7 m μ) is not strong in flames and has not been used. Mercury is commonly determined at this wavelength by atomic absorption, for which, however, no flame is required, as the metal is sufficiently volatile and inert at ordinary temperatures.

Aluminum: Thanks to recent investigations^{1, 44, 45, 46, 47} the flame determination of Al is now on a sound basis, with good sensitivity. See reference 4 for a spectrogram. Various additives are used for enhancing the otherwise weak spectrum.

Gallium, Indium, Thallium: With their simple, strong flame spectra, these elements are admirably suited for flame analysis. Still, the literature is scanty. Dean¹ reviews the chief contributions. See reference 4 for a spectrogram of In, showing the weak bands of InO. There are some very recent reports on the practical flame determination of these three metals,^{48, 49} and Lagos⁵⁰ determined them in uranium. Bulewicz and Sugden⁵¹ made a valuable study of the equilibria between Ga, In, Tl and their hydroxides, oxides, and hydrides in the flame.

Silicon: The spectrum of SiO can be excited in the flame, but there are no studies of the analytical flame photometry of this element, nor is it detectable by absorption.

Germanium: The chemiluminescent spectrum (see *Solvent*, p. 348) is excited in air-hydrogen with alcoholic solvent, the detection limit being 5 ppm.²⁵ The high specificity recommends the flame for Ge, despite the moderate sensitivity.

Tin: The resonance lines and the complex band spectrum of SnO (see references 4 and 6 for spectrograms) are rather weak in the usual flames. Oxycyanogen excites the lines well.¹⁷ But the most convenient source is the air-hydrogen-alcohol combination discussed above. Lead is now commonly determined in

gasoline (see article on "Petroleum Industry Applications, p. 365"). For reviews, see references 1 and 4.

Nitrogen, Phosphorus, Arsenic, Antimony, Bismuth: Refer to the earlier remarks on N, P, As. Air-hydrogen with alcohol provides by far the best flame emission source for As, Sb, and Bi. See also the spectrograms of Bi in reference 4. The best detection limits are about 1 ppm for P at 246.4 m μ , 2 ppm for As at 235.0 m μ , 0.5 ppm for Sb at 231.1 m μ , and 1 ppm for Bi at 223.0 m μ .

Sulfur, Selenium, Tellurium, Polonium: Several good indirect methods have been used for sulfate (see above). Durie⁵² pointed out that fluorine flames are very sensitive to sulfur; bands of S₂ appear in fluorine-hydrogen and bands of CS in fluorine-hydrocarbon flames. These, however, are not yet practical.^{1, 4} Selenite and tellurite might be determined by their quenching effect on calcium.³⁹ Although flame spectra of selenium (Se₂, SeO) are known, no work on its analytical flame photometry has been reported. On the other hand, the arc spectrum of Te is emitted in air-hydrogen with alcohol²⁵; the intensity has not been measured but should be usefully high. The extensive band spectrum of TeO is best seen in air-hydrogen with aqueous solutions.²⁵ The wavelengths and emitting species have only recently been reported.⁵³ Polonium has not been studied in the flame; it would probably emit a good chemiluminescent spectrum.

Halogens: See remarks under *Indirect Methods*, p. 357. Apparently only iodine emits flame bands useful for direct analysis. For a very recent study, see reference 54. The data in Table 1 are estimated from the results of Ohyagi⁵⁵; the IO bands are emitted only from an aqueous iodate solution. Quite probably astatine would show an interesting flame spectrum, but it is too short-lived for flame determination.

REFERENCES

1. DEAN, J. A., "Flame Photometry," McGraw-Hill, New York, 1960.

2. HERRMANN, R., AND ALKEMADE, C. T. J., "Flammenphotometrie," Springer, Berlin, 1960.
3. HERRMANN, R., "Chemical Analysis by Flame Photometry," Interscience, New York, 1961.
4. GILBERT, P. T., JR., "Analytical Flame Photometry: New Developments," in "Symposium on Spectroscopy," Am. Soc. Testing Materials, Spec. Tech. Publ. 269 (1960).
5. WALSH, A., "The Application of Atomic Absorption Spectra to Chemical Analysis," in "Advances in Spectroscopy," Vol. II, Interscience, New York, 1960.
6. MAVRODINEANU, R., AND BOITEUX, H., "L'Analyse spectrale quantitative par la flamme," Masson, Paris, 1954.
7. KELLEY, M. T., et al., *Anal. Chem.*, **31**, 178 (1959).
8. EDGERTON, J. H., et al., *Anal. Chem.*, **28**, 557 (1956).
9. McCOWN, J. J., et al., *Proc. Hot Labs. and Equip. Conf.*, 7th, Cleveland, 1959, p. 219.
10. GILBERT, P. T., JR., U. S. Patent 2,714,833 (1955).
11. FOSTER, W. H., JR., AND HUME, D. N., *Anal. Chem.*, **31**, 2028 (1959).
12. HERRMANN, R., AND SCHELLHORN, H., *Z. angew. Phys.*, **7**, 572 (1955).
13. WEICHELBAUM, T. E., AND VARNEY, P. L., *Proc. Soc. Exptl. Biol. Med.*, **71**, 570 (1949).
14. WARREN, R. L., *J. Sci. Instr.*, **29**, 284 (1952).
15. WARREN, R. L., "A versatile micro-sample flame spectrophotometer," Colloquium Spectroscopicum Internationale VIII, Lucerne, 1959.
16. Coleman Instruments, Inc., Maywood, Ill., Bulletin 231A (1954).
17. GILBERT, P. T., JR., "Oxycyanogen flame photometry," Pittsburgh Conf. on Anal. Chem. and Appl. Spectroscopy, 1958. Reprint available from Beckman Instruments, Inc., Fullerton, Calif.
18. FUWA, K., et al., *Anal. Chem.*, **31**, 1419 (1959).
19. Technicon Instruments Corp., Chauncey, N. Y., "Continuous automatic flame photometry with the AutoAnalyzer," (1959).
20. GILBERT, P. T., JR., "The design of flame emission and absorption sources," East N. Y. Regional Meeting, Am. Chem. Soc., New York, Nov. 1960.
21. EXLEY, D., AND SPROAT, D., *J. Sci. Instr.*, **35**, 202 (1958).
22. BAKER, M. R., AND VALLEE, B. L., *Anal. Chem.*, **31**, 2036 (1959).
23. FUWA, K., et al., *Anal. Chem.*, **31**, 2039 (1959).
24. KNISELEY, R. N., FASSEL, V. N., AND CUREY, R. H., "Flame spectroscopy of the rare earth elements," Pittsburgh Conf. on Anal. Chem. and Appl. Spectroscopy, 1960. To be published in *Spectrochim. Acta*.
25. GILBERT, P. T., JR., Flame Seminar, 11th Annual Symposium on Spectroscopy, Soc. Appl. Spectroscopy, Chicago, June 23, 1960.
26. ALKEMADE, C. T. J., Thesis, University of Utrecht, 1954.
27. TELOH, H. A., "Clinical Flame Photometry," Thomas, Springfield, Illinois, 1959.
28. GILBERT, P. T., JR., "Flame Spectra of the Elements," Bulletin 753, Beckman Instruments, Inc., Fullerton, Calif. (1959). New edition to appear in 1960.
29. WATANABE, H., AND KENDALL, K. K., *Appl. Spectroscopy*, **9**, 132 (1955). Available as Reprint R-79 from Beckman Instruments, Inc.
30. RAINS, T. C., et al., *Anal. Chim. Acta*, **22**, 315 (1960).
31. MARUYAMA, M., AND SENO, S., *Bull. Chem. Soc. Japan*, **32**, 486 (1959).
32. MALINOWSKI, J., *Chem. Anal. (Warsaw)*, **3**, 549 (1958).
33. ÁDÁM, J., AND ETTRE, K., *Magyar Kém. Folyóirat*, **63**, 206 (1957).
34. BOVALINI, E., et al., *Ann. chim. (Rome)*, **49**, 1046 (1959).
35. DAVIS, S., AND SIMPSON, J. H., JR., *J. Biol. Chem.*, **219**, 885 (1956).
36. CULLUM, D. C., AND THOMAS, D. B., *Analyst*, **84**, 113 (1959).
37. BRITE, D. W., *Anal. Chem.*, **27**, 1815 (1955).
38. PINTA, M., Thesis, University of Paris, 1952.
39. MALINOWSKI, J., et al., Part II, Report no. 110/VIII, Polish Academy of Sciences, Institute for Nuclear Research, Warsaw, 1959. (*Nuc. Sci. Abstr.*, **14**, no. 5164).
40. STRAUB, W. A., Thesis, Cornell University, 1958.
41. ŘEZÁČ, Z., AND DVOŘÁK, J., *Z. anal. Chem.*, **174**, 96 (1960).
42. Oak Ridge National Laboratory, ORNL-2866 (1960).
43. GIDLEY, J. A. F., AND JONES, J. T., *Analyst*, **85**, 249 (1960).
44. ESHELMAN, H. C., et al., *Anal. Chem.*, **31**, 183 (1959).
45. DEBRAS-GUÉDON, J., AND VOINOVITCH, I., *Compt. rend.*, **249**, 242 (1959).
46. SCHMIDT, W., KONOPICKY, K., "The specific enhancement of aluminum bands by fluoride ions," *Z. anal. Chem.*, in press (1960).
47. SCHMIDT, W., AND KONOPICKY, K., "New possibilities of flame photometry," *Z. anal. Chem.*, in press (1960).
48. BODE, H., AND FABIAN, H., *Z. anal. Chem.*, **170**, 387 (1959).

49. MALINOWSKI, J., *et al.*, Report no. 113/VIII, Polish Academy of Sciences, Institute for Nuclear Research, Warsaw, 1959.
50. LAGOS, A. E., p. 307, vol. 8, of *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, Geneva, 1955; published by Columbia Univ. Press, N. Y., 1956.
51. BULEWICZ, E. M., AND SUGDEN, T. M., *Faraday Soc. Trans.*, **54**, 830 (1958).
52. DURIE, R. A., *Proc. Phys. Soc. (London)*, **63A**, 1292 (1950).
53. HARANATH, P. B. V., *et al.*, *Z. Physik*, **155**, 507 (1959).
54. DURIE, R. A., *et al.*, *Can. J. Phys.*, **38**, 444 (1960).
55. OHYAGI, Y., *Science of Light*, **7**, 14 (1958).

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NEUTRON ACTIVATION PRODUCTS ESTIMATION: BORON-10 BURNUP*

To test the effect of neutron bombardment on burnable poison and control rod materials such as alloys of zirconium-boron-10, Zircaloy-boron-10, and steel-boron-10, accurate burnup values were required. As the neutron flux values were not known with sufficient accuracy to permit calculation of boron-10 burnup, an empirical determination became necessary.

Several methods of determination based on the boron-10 (n, α) lithium-7 reaction were possible. For example, mass spectrometric determination of the boron-11-boron-10 ratios before and after irradiation was used as a measure of boron-10 burnup. A second method involved the vacuum fusion of the sample with the consequent evolution of the helium produced by the n, α reaction. The composition of evolved gases was determined by mass spectrometric analysis. A third approach depended on the estimation of the actual lithium produced.

The determination of boron-10 burnup in boron carbide has been made by each of the methods described.

The data indicate that compatible results

* Abridgement of paper in *Anal. Chem.*, **30**, 2006 (1958); per permission.

were obtained by each of the methods. The last method, lithium determination, was chosen because it appeared most readily adaptable to the highly radioactive samples being considered.

The use of flame photometry for the determination of lithium in a variety of materials is well established.^{2, 4} Direct determination of lithium in the solution of the dissolved alloys by this technique was considered. However, it was impractical to install a remotely operated flame photometer. It was necessary, therefore, to reduce the radioactivity to safe handling levels prior to the "cold lab" lithium determination. For this purpose, a single precipitation of the hydrolyzable metal ions—i.e., iron, zirconium, etc.—by ammonia proved satisfactory in scavenging the radioactive species.

The experimental results show that the supernatant solutions, after the precipitation, contain the lithium being sought and, in addition, are sufficiently low in activity to permit routine handling. The precipitation step by the remote operation is simple. Filtration is unnecessary because an aliquot may be taken from the supernatant solution without prior removal of the precipitate.

Flame Photometric Reference Curve. Interferences to flame photometric analysis arise from the excess ammonia and the ammonium salts of the dissolution acids present in the supernatant solutions from the precipitation. In addition, interferences may be expected from materials not removed by the precipitation, and, to a minor extent, from reagent impurities. There is the additional consideration of lithium impurity in the alloys being studied and in the reagents. No attempt was made to evaluate the extent of interference of each of the possible factors. Instead, both the interference and the blank problems were solved by the preparation of a separate reference curve to correspond to each alloy tested. This was done by treating samples of the unirradiated, but otherwise representative, metals through step 4, the

settling of the gel. Aliquots of the supernate were removed and lithium nitrate was added to them to give lithium concentrations, after dilution, of 0, 2, 4, 6, 8, and 10 p.p.m. The volume of aliquot chosen was such as to give a concentration of supernatant constituents in these standard solutions identical to that obtained for a given size of actual sample.

The photometric gain settings were adjusted to give galvanometer readings of 0 for the 0-p.p.m. and 100 for the 10-p.p.m. standard.³ Galvanometer readings for 2-, 4-, 6-, and 8-p.p.m. standards were then obtained. The readings were plotted against lithium concentration to give the reference curve, which, when obtained in this fashion, will compensate for both the interferences and lithium blanks to be encountered in an irradiated sample.

Efficiency of Lithium-Hydrous Oxide Separation. The ammonia precipitation produced a voluminous gel which could have occluded the lithium. The results, however, indicate a clean-cut separation of the lithium from the hydrous oxides and give the overall accuracy of the method. The results were obtained by adding a solution of lithium nitrate to tabs of the various metals under consideration. The metal tabs were dissolved and the lithium was analyzed as described under procedure. The concentrations of lithium relative to sample size were chosen to cover the expected ranges of boron-10 concentration (0.2 to 1.5%) and burnup ranges (30 to 100%) expected for the radioactive samples.

The accuracy of the complete procedure could not be established, as no irradiated samples of accurately known burnup were available. Although the neutron fluxes maintained during the radiation period were not known exactly, an approximate burnup value could be calculated for the samples submitted for lithium analysis. These calculated values along with the values obtained experimentally are shown in Table 1. The compatibility of the two sets of results in-

TABLE 1. COMPARISON OF CALCULATED AND EXPERIMENTAL BURNUP VALUES FOR BURNABLE POISON ELEMENTS

Sample	Burnup, %	
	Calcd.	Exptl. (Li analysis)
Zirconium-B-10	44	33.8
	52	47.7
Stainless steel-B-10	99	100.0
	98	99.0
Zircaloy-B-10	70	78.6
	65	72.0

dicates that no gross errors are included in the experimental procedures.

Effect of Boron on Lithium Flame. A standard lithium curve was prepared with a sample devoid of its hydrolyzable ions, corrected for all interferences except boron.

Because of the burnup process, the boron concentration in a sample may decrease from 2% in an unirradiated sample to 0% in a completely burned-up sample. Although the main boron flame emission at 548 $m\mu$ would not be expected to interfere with lithium at 671 $m\mu$, the effect of boron was nevertheless checked. A known amount of lithium nitrate was added to the appropriate sample of zirconium containing 0, 0.5, and 1.5% of boron-10. After the procedure was carried out as described, the galvanometer readings were referred to a standard curve obtained with a zirconium sample containing 2% of boron.

The results indicate that boron in the concentrations encountered does not affect the flame photometric determination of lithium within the experimental error ($\pm 5\%$ relative standard deviation).

Accuracy

The accuracy of the burnup determination is probably somewhat below that indicated by the results shown for the lithium recovery, as the burnup value includes errors that may occur in the remote-controlled opera-

tions as well as in the estimation of the boron present in the unirradiated sample. It is felt, however, that these errors are not of great significance and the over-all accuracy of the procedure is on the order of 5%.

Calculations

The calculations can be summarized by means of the formula:

% burnup =

$$a \times b \times 200 \times 10/7 \times 10/c$$

where

a = lithium in γ /ml. obtained by referring galvanometer readings to the standard curve

b = dilution factor. Correction for any dilutions, exclusive of the original one to 200 ml., necessary to bring the lithium concentration to the proper range

c = weight of B-10, in γ , found in an equal weight of the unirradiated material

Conclusions

A method has been described by which the boron-10 burnup in stainless steel-boron-10, zirconium-boron-10, and Zircaloy-boron-10 samples may be determined by the flame photometric analysis of the lithium produced by neutron irradiation. For samples containing boron-10 in the range 0.2 to 1.5%, burnup values have been determined with a precision of $\pm 5\%$ relative standard deviation.

REFERENCES

1. Corning Glass Works, Optical Sales Department, Corning, N. Y., "Glass Color Filters," 1948.
2. HORSTMAN, E. L., *Anal. Chem.*, **28**, 1417 (1956).
3. Perkin-Elmer Corp., Norwalk, Conn., Instruction Manual, Flame Photometer Model 52A.
4. STRANGE, E. E., *Anal. Chem.*, **25**, 650 (1953).
5. VALOVAGE, W. D., KPAL-1403, "Effect of Irradiation on Hot-Pressed Boron Carbide," p. 17, Nov. 15, 1955.

D. DUTINA

PAINT INDUSTRY APPLICATIONS

In the paint industry, flame photometry may be used for the detection and determination of most metals present in driers, paint vehicles, resins and pigments.

In general the advantages of the qualitative applications are the speed of the analyses, the little experience required to obtain and interpret results, and the high reliability of the results due to the fact that the emitted lines are specific for each element. Also sodium and potassium, which are difficult to detect by most methods, can be detected in extremely small amounts. A few metals, however, emit so little that they cannot be detected at all or can be detected only when present in large amounts.

When the metal contents of many samples of similar composition are to be determined, flame photometry has the advantage of speed, many determinations being possible within a matter of minutes after standard solutions and calibration curves have been prepared. Precision and accuracy of results are usually adequate. Considerable time is usually necessary to determine the optimum concentration of the standard solution (sufficiently dilute to obtain a reasonably linear relationship between concentration and emission without having a high ratio of background emission and/or noise to total emission) and to prepare the calibration curves. Thus the time advantage is usually lost unless several samples are to be analyzed.

One of the more ideal applications for the flame method is determination of the metal contents of metallic driers (metal soaps of organic acids). The metal contents of lead, cobalt, manganese and calcium driers may be determined satisfactorily. The sample may be dissolved directly in an organic solvent and diluted with the solvent to the desired concentration. Precision of the method can be maintained within one per cent relative error. Accuracy of the method is limited only by the precision of the method

and by the accuracy with which the metal contents of the standard or reference driers can be determined by other methods. Probably no other method combines the speed, precision and reliability of the flame method for the determination of the metal contents of driers.

Another similar use of flame photometry is the detection of the metals present as driers in the vehicles separated from paint. Lead, cobalt, manganese and calcium in the amounts usually present can be detected. Semiquantitative determinations are possible. The determination of lead is especially useful since chemical extraction of the lead is extremely time consuming.

In the qualitative analysis of pigments, nearly all the metals, except zinc, of the acid soluble pigments can be detected rapidly. The only sample preparation necessary is

treatment of the pigment with dilute hydrochloric acid and removal of the acid insoluble portion of the pigment by filtration. Quantitative determination of the metals is also possible if the approximate composition of the pigment is known.

Detection and determination of many impurities remaining in resins and vehicles resulting from manufacturing processes are feasible. Sodium in epoxy resins is an example.

PAUL J. SECREST

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Analytical determinations of inorganic elements in a wide variety of sample types are required in the petroleum industry, either for routine control or for research purposes. Flame photometry is an excellent method for many of these determinations. It offers

TABLE 1. SAMPLE TYPES AND REFERENCE NUMBERS

Element	Catalysts	Chemical additives and organic compounds	HPD*	LPD*	Misc*
Barium	1, 32	32	4, 10, 20, 32		32
Boron		7, 32	7	12, 32	
Calcium		14, 32	4, 10, 12, 16, 27, 32	32	14, 21, 32
Chlorine (as chloride)		22			22
Chromium	14				14
Copper			29, 32	18, 32	14, 32
Iron			16, 30, 32		14, 21, 32
Lead			30, 32	6, 8, 12-15, 19, 24, 25, 28, 32	14, 32
Lithium	32	32	10, 32	32	32
Magnesium		32		32	14, 21, 32
Manganese		32	29, 30, 32	28, 32	14
Nickel			30		14
Nitrogen	1, 31, 32	17			
Phosphorus		5			
Potassium		32	3, 32	32	32
Sodium		32	2, 3, 11, 32	32	14, 21, 32
Strontium	1, 26, 31, 32	32	4, 10, 16		32
Tin			16		14
Vanadium			14, 30		

* HPD (heavy petroleum distillate) for purposes of this tabulation includes crude oils, residual oils, refinery feed stocks, blending stocks, and finished lubrication oils both new and used. LPD includes refinery feed stocks, blending stocks and finished gasolines. Miscellaneous includes a variety of water samples, deposits, greases, asphalts and others including special samples obtained through research.

FLAME PHOTOMETRY

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1. Corning Glass Works, Optical Sales Department, Corning, N. Y., "Glass Color Filters," 1948.
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the advantages of speed, precision and the direct determination of metals in organic solutions.

Flame photometric procedures have been used for the qualitative and semiquantitative determination of metals in oils^{4, 14, 16, 20} and quantitative determinations of metals in oils and other samples. Table 1 lists sample types, elements determined and the corresponding literature references.

Applications given in the tabulation do not include those more properly classified in other industries. During exploration for oil, the production of oil, and the manufacture of petrochemicals, flame photometric methods used in the agriculture and mineral industries may be employed by the petroleum industry. Methods used in clinical laboratories or in the analysis of industrial waters may also be employed. Bibliographies for such methods are given by Burriel-Martí and Ramírez-Muñoz,⁹ and Mavrodineanu.²³

Flame photometers have become increasingly important as analytical tools in petroleum laboratories; today they are standard equipment. Flame photometers are often employed to provide faster and more precise determinations in laboratories having emission spectrographs. As flame photometry develops, it will become increasingly valuable to the petroleum industry in future analytical and research applications.

REFERENCES

1. ALEKSANDROV, S. N., SHMULYAKOVSKI, YA. E., AND ALEKSEEV, S. A., *Khim. i. Tekhnol. Topliva*, No. 4, 68-72 (1956); in Russian.
2. "ASTM Standards on Petroleum Products and Lubricants," Am. Soc. Testing Materials, Philadelphia, Pa., p. 478, 1958.
3. Am. Soc. Testing Materials, Proposed Method of Test for Sodium and Potassium in Residual Fuel Oil, April 28, 1958 (unpublished).
4. Beckman Instruments Inc., Beckman Tech. data sheet DU-47-M (T), Sept., 1955.
5. BRITE, D. B., *Anal. Chem.*, **27**, 1815 (1955).
6. BUELL, B. E., "Special Problems in the Determination of Tetraethyllead in Gasoline by Flame Photometry," Am. Soc. Testing Materials, Spectroscopy Symposium, San Francisco, Calif., October 13, 1959.
7. BUELL, B. E., *Anal. Chem.*, **30**, 1514 (1958).
8. BURRESS, G. T., AND GRANT, J. A., Rapid Analysis for Tetraethyllead in Gasoline by Flame Photometer, Am. Chem. Soc., Atlantic City, Sept. 15, 1952.
9. BURRIEL-MARTÍ, F., AND RAMÍREZ-MUÑOZ, J., "Flame Photometry," Elsevier Publishing Co., Amsterdam, 1957; translated from the original Spanish manuscript by W. C. Darwell. (909 references.)
10. CONRAD, A. L., AND JOHNSON, W. C., *Anal. Chem.*, **22**, 1530 (1950).
11. CURTIS, R. E., AND SCOTT, R. W., *Anal. Chem.*, **26**, 1851 (1954).
12. DUBOIS, H. D., AND BARIEAU, R., Improved Flame Photometry by Direct Recording Study of Selected Flame Area Emission, Am. Pet. Institute, Los Angeles, Calif., May 12-15, 1958.
13. Ethyl Corporation, method EAM 90-58, to be published as information by Am. Soc. Testing Materials.
14. GILBERT, P. T., JR., *Ind. Labs.*, **3**, 41 (1952) Beckman Reprints R-56 and R-60.
15. GILBERT, P. T., JR., ASTM Spec. Tech. Publ. 116, 67 (1951).
16. GLEASON, S. I., AND HOLD, GAYLORD, Beckman Bull., No. 16 (1955).
17. HONMA, MINORU, AND SMITH, C. L., *Anal. Chem.*, **25**, 459 (1954).
18. JORDAN, J. H., *Pet. Refiner*, **33**, 158 (1954).
19. JORDAN, J. H., *Pet. Refiner*, **32**, 139 (1953).
20. MAHN, I., AND HERBERT, F., A Rapid Method for the Determination of Calcium and Barium in New Lubricating Oils, Am. Chem. Soc., Cincinnati, Ohio, April, 1955.
21. MARSH, G. E., *Applied Spectroscopy*, **10**, 8 (1956).
22. MARSH, G. E., Flame Photometric Determination of Chlorides, Pittsburgh Conf. on Anal. Chem. and Appl. Spectroscopy, Pittsburgh, Pa., March 2, 1956.
23. MAVRODINEANU, R., "Bibliography on Analytical Flame Spectroscopy," *Applied Spectroscopy*, **10**, 2-28, Nos. 2 and 3 (1956).
24. MEINE, W., *Erdöl. u. Kohle*, **8**, 711 (1955); in German.
25. OKADA, T., UEDA, T., KOHJIMA, T., *Bunko, Kenkyu*, **4**, 30 (1956); in Japanese.
26. PAGLIASSOTTI, J. P., AND PORSHE, F. W., *Anal. Chem.*, **24**, 1403 (1952).
27. MOBERG, M. L., WAITTMAN, V. B., ELLIS, W. H., AND DUBOIS, H. D., ASTM, Spec. Tech. Publ., 116, 92 (1951).

28. SMITH, G. W., AND PALMBY, A. K., *Anal. Chem.*, **31**, 1798 (1959).
29. VALLEE, B. L., Report on the Cyanogen-Oxygen Flame Spectrometer for Petroleum Analysis, Research report to the Am. Pet. Institute, May, 1958.
30. WHISMAN, M., AND ECCLESTON, B. H., *Anal. Chem.*, **27**, 1861 (1955).
31. ZAIDMAN, N., AND ORECHKIN, D., *Novosti, Neftyanof Tekh., Neftepererabotku*, 1955, No. 5, 25-30; in Russian. cf. *C.A.*, **51**, 5625 d (1957).
32. Unpublished methods used by various oil companies.

BRUCE E. BUELL

PLANT MATERIALS

The chemical analysis of plant materials is of great scientific and practical interest in determining availabilities of different fertilizer elements and in characterizing texture, appearance, and cooking quality of fruits and vegetables. The conventional methods of chemical analysis are not rapid enough to meet the output requirements of many research programs. The rapidity with which the analytical determinations can be made and the small sample required are the principal advantages of the flame photometric method of analysis.

A brief description of the principle of flame photometry, types of instruments, and their special adaptations for plant analysis follows.

The basic principle of flame photometry rests on the fact that salts of metals when introduced into a hot flame emit radiations that are characteristic for each metal. Some of these radiations may be perceived by the eye, as the yellow color of sodium and the green color of copper, while others give radiations of short wave lengths that are not perceived by the eye. The emission of radiant energy has two aspects; (a) the qualitative, characterized by one or more lines or bands in the spectrum, and (b) the quantitative, characterized by the intensity of the emission, related to the concentration of the

element in solution. The function of the flame photometer is to *isolate* the spectral line or bandhead of the desired element in a solution in mixture with other elements and to measure quantitatively its *emission intensity* as related to its concentration.

The essential components that characterize the operations and capabilities of flame photometers are: (a) the atomizing device for converting the solution of the analytical material into minute uniformly-sized droplets for steady flow into the flame; (b) the flame source produced by the burning of various fuels in mixtures with air or oxygen for the excitation of the elements to luminescence (each source having certain temperature and flame background characteristics); (c) the optical system for the dispersion of the mixed radiant energy and for the isolation of the desired spectral lines or bands by the use of color filters or prisms, with exit slits; (d) appropriate photocells for transforming the radiant energy into electrical energy; (e) an electrical circuit for the amplification and measurement of the intensity of the radiation. The intensity measurement can then be converted to concentration from a previously made curve in which emission is plotted against concentration of standard solutions.

Types of Flame Photometers. The more popular and less expensive types of commercially available flame photometers are those supplied with air-propane or air-gas grid type burners that produce a flame temperature of 1900-2000°C and that are designed primarily for determinations of sodium and potassium. For the separation of the desired spectral bands, some of these instruments are provided with glass prisms (Perkin-Elmer); others, with appropriate color filters (the direct-reading Beckman). The Perkin-Elmer instrument is also equipped as a double-beam circuit for use with lithium as an internal standard by which method errors caused by fluctuations in gas pressure, droplet size and ion interference are minimized.

FLAME PHOTOMETRY

Apart from being cheaper, the simple type of instrument also has the advantage that it can be manipulated by less well-trained personnel; and, where plant analysis consists predominantly or entirely of determinations of sodium and potassium, this type of instrument is entirely satisfactory. For many problems, however, which also require the determination of calcium and magnesium and the micronutrients copper and manganese, the glass prism photometers, having a spectral dispersion between 380 and 850 $m\mu$, and the filter instruments are totally inadequate.

For the determination of magnesium, iron, and copper it is necessary that the spectral dispersion be extended below the visible region, as is done by the Beckman DU quartz prism monochromator, or its equivalent. The Beckman flame photometer is supplied

with integral aspirator-burners for use of oxyacetylene or oxyhydrogen flame, giving temperatures of 3100 and 2800°C, respectively. The adjustable slit width makes it possible to isolate closely adjacent wave lengths or bandheads, which cannot be attained by the use of filter instruments. Furthermore, the photomultiplier tube attachment increases the sensitivity of the instrument, thereby making possible the use of very narrow slits for the isolation of closely adjacent spectral lines. For the most advantageous use of the Beckman DU flame photometer, however, the operator must possess some skill and judgment in obtaining proper instrumental adjustments.

The following adjustments require special emphasis: (a) selection of the spectral line or band peak that will provide the least interference from other emission lines or bands, continua, and flame background emission; (b) selection of the best oxygen and fuel pressure combination that will give maximum net emission; (c) selection of the narrowest slit consistent with sufficient radiation when the photomultiplier and monochromator are adjusted at optimum operating sensitivities.

Preparation of Sample. Aqueous and ammonium acetate extractions of plants have been used for the direct flame photometric determinations of sodium and potassium contents. More generally, however, the ashed plant material is dissolved in dilute hydrochloric acid and used for the determination of several elements. The ash may be obtained by incineration in an electric furnace at a temperature not exceeding 500°C or by the more commonly used method of "wet ashing" in a mixture of nitric and perchloric acids. For most purposes a 1-to-2 gram sample of the plant material in a final solution volume of 100 ml will supply the best average concentrations for the direct flame photometric determinations of calcium, magnesium, potassium, and sodium. For determination of micronutrient elements a 3-to-5 gram sample should be taken. The

TABLE 1. D VALUES OF IMPORTANT PLANT ELEMENTS AT DIFFERENT WAVE LENGTHS USING BECKMAN DU FLAME PHOTOMETER AND MULTIPLIER ATTACHMENT

Element	Wave Length,	D value
	$m\mu$	ppm
Calcium	422.7	0.08
	554	0.22
Magnesium	285.2	0.20
	371	0.10
Sodium	589	0.001
	330	50.0
Potassium	768	0.05
	404	1.7
Barium	515	1.0
	873	0.3
Manganese	403.1	0.01
	561	0.20
Strontium	461	0.07
	606	0.30
Copper	324.7	0.6
	327.4	1.0

acid solution of the ash that has been freed of silica is commonly designated as solution A. With proper sample preparation, the same solution can be used for indirect flame photometric determinations of sulfate and phosphate; the sulfate, by precipitation as barium sulfate followed by the flame photometric determination of the excess barium concentration; the phosphate, by its depressant effect on flame photometric emission intensity of calcium. The phosphate, however, may be more conveniently determined by one of the colorimetric procedures on a small aliquot of solution A.

An outline of sample solution with provisions for the removal of perchlorate, sulfate, phosphate, iron, and aluminum follows:

(a) Digest a 1 or 2-gram sample of plant material in a mixture of nitric and perchloric acid, followed by one hour of boiling in perchloric acid. (b) Evaporate excess perchloric acid, bring into solution in (1 + 1)HCl, and evaporate on warm part of hot plate. (c) Dissolve residue by warming in 5 ml of 1N HCl, dilute with 75 ml of H₂O, and boil gently to dissolve salts. Precipitate sulfate by addition of enough 1/16N BaCl₂ to give a 5 to 10 ml excess of the reagent. Digest and let stand overnight. (d) Without removing the BaSO₄, add 10 ml of a 2N acetate buffer which has been adjusted to pH 4 with ammonia, 5 ml of 0.5N FeCl₃ in 0.5N HCl, and add 1N NH₄OH in the quantity required to neutralize the combined additions of the 1N HCl and the FeCl₃. Digest in covered beakers on hot plate at gently boiling temperature to obtain a good flocculation of the reddish brown precipitate (15–30 min). Remove from hot plate, transfer to 100-ml volumetric flasks, cool to room temperature, fill to mark with H₂O, mix and filter through 12.5-cm folded paper into polyethylene bottles. The filtrate contains the residual barium from the sulfate precipitation, calcium, magnesium, sodium, potassium, and manganese. Iron, aluminum, and phosphate are contained in the precipitate.

The solution that has been freed of the elements Fe, Al, P, and S may be denoted as solution B.

Spectral Lines and Bands, and Detection Limits of Elements. In the flame, the solution of a metal simultaneously exhibits several spectral emission lines and bands which have different emission intensities. The line or band peak that shows the highest emission intensity is termed the *persistent line* and is usually chosen as the identifying and analysis wave length for that metal. In flame photometry manuals the relative emission intensities of the different lines of the same metal and of different metals are expressed by their detection limits, *D values*. The *D values* bear an inverse relation to the relative emission intensities. They are defined as the least concentrations of an element that will be detected above the solvent flame background. The *emission intensity* is the total emission less that of the flame and cation background.

The *D values* for the most important elements in plant analysis are given in Table 2. These values have an important bearing on the minimum concentration of the elements required to hold the analysis within certain limits of error. Theoretically, for an analytical error of $\pm 1\%$, the concentration of the element should be 100 times its *D value*. As the concentration ratio is reduced, the error becomes proportionately greater. It should be noted that the *D values* given in different manuals were obtained under various conditions and are often in conflict. It is best to obtain such values with the instrumental adjustments under which the element is to be determined.

Calibration Standards and Instrumental Adjustments. The instrumental adjustments depend on the concentration range of the elements analyzed. The maximum standard concentrations that would be suitable for average plant material and the corresponding adjustments are indicated in Table 2. The preliminary instrument settings

FLAME PHOTOMETRY

TABLE 2. WAVE LENGTHS AND TENTATIVE INSTRUMENTAL ADJUSTMENTS¹ FOR PLANT MATERIAL ANALYSIS WITH BECKMAN DU FLAME PHOTOMETER AND PHOTOMULTIPLIER ATTACHMENT

Element	Standard, ppm	Wave Length, mμ	Pressure		Photomultiplier Setting	Slit Width, mm.
			O ₂ p.s.i.	C ₂ H ₂ p.s.i.		
Ca	500	422.7	10	3	1	.02-.03
Mg	100	285.2	10	5	4-5	.03-.05
K	500	767	10	3	4-5	.03-.05
Na	100	589	10	3	1	.02-.03
Ba	100	515-522 ²	10	2 ²	4-5	.03-.05
Mn	10	403-401 ²	10	5	4	.04
Sr	10	461-466 ²	10	3	4	.04-.05
Cu	10	325	10	5	4	.04-.05

¹ Other monochromator adjustments are: selector switch on 0.1; sensitivity knob about one turn from counterclockwise limit.

² Hydrogen was used with barium, in all other instances, acetylene was used.

³ Wave lengths used for background corrections, (L-H).

should be made about 15 minutes in advance of use. The calibration standards are prepared from stock solutions containing 1 gram of the metal per liter of aqueous solution of the chemically pure chloride salts. The concentration intervals are usually in steps of 20% of the maximum, with a 10% point between the zero point and the 20% point. The stock solution is pipetted into 100-ml volumetric flasks, the solvent salts are introduced to give a concentration equal to that in the sample, and filled to the mark with distilled water.

With the burner lighted and the dial set at the required wave length, the fine adjustment is made while the maximum standard is being aspirated in the flame and the slit opened wide enough so that the radiation will register on the galvanometer. Slowly turn the wave length knob in the direction that will give the greatest response (needle moving to the left) while narrowing the slit to zero the needle. Continue until the point is reached where the slightest motion either to the right or left will give a deflection of the needle to the right.

Set the T-dial on 100, the monochromator sensitivity 1 turn from counterclockwise limit; set the photomultiplier on the switch that will allow a near balance of the needle at a slit width of 0.03 to 0.05 mm. The final adjustment is made by turning the sensitivity knob. During this time two points need continual checking: one is the fuel pressure that tends to drop and needs adjustment; the other is the dark current zero adjustment. When reproducible readings have been obtained on alternate readings of maximum and zero standards, the readings on the intermediate concentrations are then obtained and plotted on coordinate paper.

Interference Effects. The most serious problem attending flame photometric analysis is the change in the emission intensity of an element when analyzed in the presence of extraneous elements or in various solution media. Any change in the emission intensity of an element from that of its standard solution is described as an *interference*. Interference phenomena caused by extraneous elements are commonly grouped under *cation* and *anion* effects. The silicate, phosphate, and sulfate ions commonly found in plant ash solution exert serious inhibiting effects on the emission of calcium, magnesium, and strontium; whereas the perchlorate ion, residual from the wet ashing, has an enhancing effect. Anion exchange resins have been used for the removal of phosphate and sulfate ions. The author prefers their removal by chemical precipitations as described in the outlined procedure. This method has the advantage that it also removes soluble aluminum which has a strong depressing effect on the flame emission of calcium.

Cation interferences are grouped according to the nature or source of interference and means of circumventing them. *Spectral or band-width interference* is due to proximity of two emission lines and the superimposing or overlapping of two band widths. The high resolving power of the monochromator is capable of isolating closely adjacent lines like those of manganese 403 mμ from potas-

sium 404 $m\mu$; but it cannot undo the direct interference from overlapping bands like those of calcium and barium at 554 $m\mu$ peaks. In such instances, other wave lengths are selected, as 423 $m\mu$ for calcium and 515 $m\mu$ for barium.

Radiation interference is a type of interference in which the interfering element shows no radiation of its own at the analysis wave length. It is encountered in the calcium flame in presence of aluminum, phosphorus, and sulfur. These interferences have been ascribed to the formation in the flame of compounds with the analysis element which are of higher vaporization temperature than the chloride. There is evidence that manganese has an effect on the emissions of calcium and strontium somewhat similar to that of aluminum. The mutual interference between sodium and potassium also comes under this designation.

Background interference comes as a result of high concentrations of sodium, potassium, and other elements in the presence of a low concentration of the analysis element. The interfering elements exert a *continuous radiation* over a wide region of the spectrum. Such an effect is found on the barium emission at 515 $m\mu$ and has been remedied by subtracting the background radiation at 522 $m\mu$ from the total emission at 515 $m\mu$. This is known as the "L-H" method of background correction and can be used only where the background is of the same magnitude at the two wave lengths used.

Complex cation effects are exemplified by the effects of sodium and magnesium on calcium emission. These elements inhibit emission at low concentrations but enhance it as the concentration of the interfering element increases. Under such circumstances the most practical remedy is the use of *compensated standards*. In this instance, the calcium standards are supplied with the approximate concentrations of sodium, magnesium, and potassium that are likely to be found in the unknowns.

Considerable work will have to be done

before the various interferences can be fully understood and remedies for their correction supplied.

The much smaller interferences obtained for the elements other than calcium indicate that many mutual cation interferences can be controlled by the use of the photomultiplier and narrow slits.

Trace Elements. Copper has been extracted from a 0.1N HCl solution with 10 ml of a solution made up by taking 1 part kerosene and 1 part chloroform containing 0.1% dithizone and then Cu determined in the oxyhydrogen flame at 324.8 $m\mu$ wave length.

Manganese can be determined photometrically in concentrations of 2 to 5 ppm in solution B.

Strontium, while not recognized as a plant nutrient, is of interest because of its content in radioactive fallout and its uptake by plants, particularly in its relation to soil liming. Flame analysis has been successfully used for its determination.

W. M. SHAW

SAMPLE FLOW EFFECT ON SPECTRAL EXCITATION

The rate of introduction of a liquid sample solution into the flame has long been recognized as one of the significant variables in flame photometry. In the past, it has been customary to enhance the sensitivity of detection of low metal ion concentrations in aqueous solution by increasing the rate of sample flow, meanwhile assuming a negligible cooling effect upon the flame. On the basis of a thermodynamic model, a relationship has been proposed which predicts the existence of optimal flow rates for maximum sensitivity of detection of inorganic ions in aqueous samples.

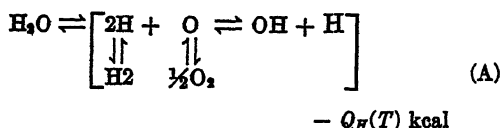
The temperature of any flame is a function of the thermal stabilities of its combustion products.⁶ If water is introduced into the flame, it deprives the flame of the energy needed to decompose the water and raise its

products to the same temperature as the products of combustion of the flame. Hence, the temperature of the flame is lowered. Quantitative estimates of the oxygen-hydrogen flame temperature changes due to the addition of water have been made by Foster and Hume³ using a modification of the hydroxide rotational temperature method developed by Broida and co-workers.² Temperature changes of up to 600°K were noted when the flow rate increased from zero to six milliliters per minute.

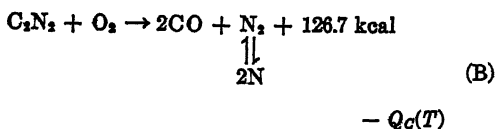
The reaction for the stoichiometric oxygen-hydrogen flame can be written.



whereas in actuality, at the equilibrium temperature, the combustion product, water, decomposes and enters into states of equilibria which can be represented by the equation



$Q_H(T)$ is the sum of the heats of reaction and of enthalpy differences for each product between the initial and final temperature per mole of water. Similarly, the equation for the cyanogen-oxygen flame can be represented by



where $Q_C(T)$ is the energy required to raise the products to temperature, T .

Modifying a Boltzmann distribution curve relating the intensity of a spectral line to the excitation potential energy and the temperature of thermal equilibrium, Baker and Vallee¹ have proposed a theoretical model where the intensity of the spectral line is directly related to the sample flow. Denoting the solvent flow as x in molar units, the proposed

intensity is written as

$$I = A x e^{-E/kT(x)}$$

where A is a constant and $T(x)$ represents the absolute temperature of the flame as a function of the flow rate x . The other symbols retain their customary meaning.

In the case of aqueous flow into the cyanogen-oxygen flame, the net reaction is written as the sum of Equations A and B, or more simply $\text{C}_2\text{N}_2 + \text{O}_2 + x\text{H}_2\text{O} \rightarrow \text{products}$. Assuming thermal equilibrium, the net Q at any temperature must be zero, or

$$126.7 - xQ_H(T) - Q_C(T) = 0$$

$Q_H(T)$ and $Q_C(T)$ are calculated from thermodynamic constants at various temperatures,^{6,7} and an empirical equation relating temperature as a function of sample flow can be fitted to the resultant plot. Substitution of the temperature function into the proposed theoretical model yields a curve which relates spectral line intensity as a function of sample flow and excitation energy, which is a constant for a particular line. The curve possesses one maximum which can be located by equating the first derivative to zero and solving for the optimal flow rate as a function of the excitation potential, E . Similar calculations can be performed for the hydrogen-oxygen flame.

Fuwa *et al.*,⁴ using a system of flame control developed earlier,⁸ have investigated the flow rate values at which maximum sensitivity was achieved for the calcium lines at 3968.5 Å and 4226.7 Å in both the cyanogen-oxygen and hydrogen-oxygen flames. Experimental data agree with the theoretical results. Foster and Hume,³ in an independent investigation of the role played by sample flow rate upon spectral line intensity, show agreement with the theoretical model in the cases of Cs, K, and Na. An exception is noted in the case of lithium where two spectral lines of two different excitation energies reach a sensitivity maximum at the same flow rate.

Such agreement between experimental evidence and theoretical considerations would suggest that the calculations could be applied to other solvents with equally successful results.

REFERENCES

1. BAKER, M. R., AND VALLEE, B. L., *Anal. Chem.*, **31**, 2036 (1959).
2. BROIDA, H. P., AND LALOS, G. T., *J. Phys. Chem.*, **20**, 1466 (1952).
3. FOSTER, W. H., JR., AND HUME, D. N., *Anal. Chem.*, **31**, 2028 (1959).
4. FUWA, K., THIERS, R. E., VALLEE, B. L., AND BAKER, M. R., *Anal. Chem.*, **31**, 2039 (1959).
5. *Ibid.*, **31**, 1419 (1959).
6. GAYDON, A. G., "The Spectroscopy of Flames," Wiley, New York, 1957.
7. GAYDON, A. G., "Dissociation Energies," Dover, New York, 1950.

FRED TIVIN

FLUOROPHOTOMETRY AND PHOSPHORIMETRY

FLUORESCENCE*

Fluorescence¹ is a process in which an atom or molecule emits radiation in the course of a transition from a higher to a lower electronic state. A more restricted definition, applicable particularly to atomic processes, excludes the special case, known as *resonance radiation*, in which the wavelength of the emitted radiation is the same as that of the exciting radiation. The term "fluorescence" is further restricted to phenomena in which the time interval between the acts of excitation and emission is small, of the order of 10^{-8} – 10^{-3} second. This distinguishes fluorescence from *phosphorescence*, where the time interval between absorption and emission may extend from 10^{-8} second to several hours.

Fluorescence is exhibited both by free atoms and by molecules; it can occur in the gaseous, liquid and solid states, although not necessarily in all three phases of the same substance. It is observed in its simplest form in the classical experiment of Lord Rayleigh, in which sodium vapor, confined in a quartz vessel at low pressure was exposed to the ultraviolet radiation from a spark between zinc electrodes. This causes the sodium vapor to glow with a yellow fluorescence corre-

sponding in wavelength to the D-line transition of sodium atoms falling from the first electronically excited state to the ground state. The absorption of the ultraviolet radiation excites the sodium atoms to high electronic energy levels. Part of this excitation energy is dissipated by collision with other sodium atoms, or the walls of the vessel, reducing the atom to its lowest electronically excited state, from which it subsequently drops to the ground state with the emission of the D-line radiation. In such atomic processes the wavelength of the fluorescent radiation is always longer than that of the exciting radiation—a generalization known as Stokes' Law. Fluorescence can occur also in molecules, but the process is more complex, since the electronic excitation and de-excitation processes may be accompanied by secondary changes in the vibrational and rotational energy of the molecule.

The relationship between the molecular structure and the fluorescence of organic compounds is less well understood than the factors determining the initial absorption process. It is important for fluorescence that the molecule not only contain a chromophoric system to absorb the exciting radiation, but also that the excited electronic system be shielded adequately from internal and external influences which would permit

* From the "Encyclopedia of Chemistry", Reinhold, 1957, p. 407.

a too rapid dissipation of the excitation energy into vibrational motion before the fluorescence re-radiation act can occur. At present it is not possible to define the type of molecular structure required to induce strong fluorescing power, but certain substituent groups, notably the $-\text{NO}_2$ group are commonly associated with a strong quenching effect on the fluorescence of any molecule to which they are attached as part of a conjugated system. Among organic compounds brilliant fluorescence is particularly associated with the phthalein structures and also with aromatic structures such as anthracene and naphthacene, which contain condensed systems of several benzene rings. Few inorganic compounds fluoresce strongly in the liquid state or in solution, but in the solid state the fluorescence of certain uranyl salts and platinoeyanides is outstanding.

In solids, fluorescence is often greatly modified by the presence of trace impurities and a considerable literature exists on the nature of such phenomena which are commonly associated with irregularities in the crystal lattice (F-centers). As examples we may note that the blue fluorescence of pure solid anthracene changes on the addition of 10^{-4} mole of naphthacene, and the resulting green fluorescence is characteristic of the naphthacene and not the anthracene molecule. Similar effects are noted in solid inorganic systems, particularly zinc sulfide, the blue fluorescence of which is greatly intensified by the addition of one part in ten thousand of cupric chloride. The application of such effects to the analysis of trace amounts of the activating substances will be apparent.

Fluorescence can also be induced by other excitation mechanisms as well as ultraviolet irradiation. The excitation of fluorescence by electron bombardment constitutes the basic process in the illumination of cathode-ray oscillograph and television screens and the excitation of fluorescence by α -, β - and γ -rays is employed in scintillation counters for the monitoring of radioactivity.

REFERENCES

1. WEST, W., "Fluorescence and Phosphorescence" in Weissberger's "Technique of Organic Chemistry," Vol. 9, New York, Interscience, 1956.

R. NORMAN JONES

FLUOROPHOTOMETRY

Of growing importance for the assay, identification and analysis of a wide variety of natural and synthetic substances, especially those of significance in the biochemical and medical fields, is the technique of fluorophotometry. Any specimen which absorbs radiation in the ultraviolet, visible or infrared ranges of the spectrum and becomes fluorescent by emission of radiation is suitable for this technique which may be more sensitive and discriminating than colorimetry or spectrophotometry (q.v.) for measurements of extremely low concentrations in macro or micro volumes of solutions. Instrumentation is of two types analogous to absorption photometry and spectrophotometry: (1) the photoelectric fluorometer, and (2) the spectrofluorometer.

In the first, simpler type of which the Farand instrument is typical, light from a mercury arc lamp providing effective ultraviolet and visible radiation is controlled by a shutter and disc-type diaphragm with varying size apertures. A separate compartment accommodates a quartz lens system, primary filter holder, a rotatable cuvette carrier table (usually for 3 cuvettes, standard, sample and blank) a second quartz lens system at right angles to the first system, and a secondary filter holder. A third compartment contains the photoelectric detecting unit. The fluorescent radiation excited in the sample by the narrow band of radiation provided by the filter is collected at right angles to the illuminating beam. The fluorescent beam is used to image the center of the cuvette on the cathode of the photomultiplier tube by means of the second quartz lens system and

secondary filter. A sensitive galvanometer or microammeter is usually provided for indication of the photoelectric current and hence intensity of the fluorescent radiation.

The more elaborate and quantitative spectrofluorometer involves the use of two monochromators (q.v.), so that the chemical constituents under investigation can be irradiated in any single chosen wavelength of the ultraviolet, visible or infrared regions, usually 220 to 650 millimicrons, through the excitation monochromator and the measurement of the resulting fluorescence likewise obtained at any chosen wavelength in these regions through an analyzing monochromator. A xenon arc source of light is commonly preferred. Of course the entire fluorescence spectrum may be scanned in this way for selection of the optimum wavelength for a constituent. The microammeter visual reading may be replaced by automatic recording peaks and spectra on such recorders as the Varian strip chart or Brown Elektronik, or by an oscilloscope (DuMont Type 304-A). Farrand instruments provide arrangements for reflectance or transmittance measurements, use of solid samples, and measurements in paper chromatography.

Numerous recent papers report the results of fluorometric measurements on steroids, estrogens, amino acids, serotonin (in the brain), epinephrine, reserpine, tranquilizing alkaloids, and many other compounds of pharmacological and biological interest. Specific data for a long list of these compounds on activation peak and fluorescent peak wavelengths are presented in the references.

REFERENCES

1. DUGGAN, D. E., BOWMAN, R. L., BRODIE, B. B., AND UDENFRIEND, S., *Arch. Biochem. and Biophys.*, **68**, No. 1, May 1957.
2. UDENFRIEND, S., DUGGAN, D. E., VASTOR, B. M., AND BRODIE, B. B., *Jour. Pharmacol. Exptl. Therapeutics*, **120**, No. 1, May, 1957.
3. Farrand Optical Co., Inc., N. Y., Brochures and Tables from above articles.

G. L. CLARK

PHOSPHORIMETRY*

Phosphorimetry is a means of chemical analysis based on the nature and intensity of the phosphorescent light emitted by an appropriately excited molecule. Many organic molecules containing multiple bonds phosphoresce if excited by radiant energy of suitable frequency. A few of the common organic molecules that can be made to phosphoresce are: benzene, naphthalene, anthracene, aniline, nitrobenzene, benzaldehyde, benzophenone, acetophenone, toluene, phenol, fluorescein and their derivatives. Inorganic molecules such as CO_2 and SO_2 are also phosphorescent.

Each phosphorescence is unique in regard to its frequency, lifetime, quantum yield, and vibrational pattern, and such properties are used for qualitative identification. The correlation of intensity with concentration can serve as a basis for quantitative measurement. The resolution of mixtures of phosphorescent substances is possible in three ways: (1) by selective excitation, (2) spectroscopically, and (3) phosphoroscopically on the basis of the phosphorescent lifetimes.

Substances that phosphoresce may be divided into two classes, based on the mechanism by which their phosphorescences are produced. In the first group are mineral, or crystal, phosphors. In this case the individual molecule is not phosphorescent, but the ability to emit an afterglow is associated with the return of an electron to an impurity site in the crystal, following ionization through the process of photon absorption. As this type of phosphorescence cannot be ascribed to a definite substance, phosphorescences of this class are not considered suitable for this type determination. In the second class the emission is attributed to a definite molecular species. It is

* From "Encyclopedia of Chemistry Supplement," Reinhold, New York, 1958, p. 224

with such compounds that this method is utilized.

Phosphorescence is produced in molecules by the absorption of radiant energy of a frequency within the normal absorption band of the molecule—usually in the ultraviolet region of the spectrum. Two of the many possible end results are fluorescence and phosphorescence produced by the excitation of an appropriate electron energy level of the molecule. In order to observe the phosphorescences of such excited molecules in solution it is necessary to dissolve them in a suitable solvent which, upon cooling to low temperatures, forms a rigid transparent glass. The role of the rigid medium is to prevent the collisional deactivation of molecules in the excited phosphorescent (triplet) electron levels before the molecule emits. One such solution (EPA) widely used consists of a mixture of ethyl ether, isopentane and ethanol.

The phosphoroscope is of a modified Becquerel type and consists of two slotted disks mounted to a common shaft and driven at a selected speed by a synchronous motor. The disks are so arranged that openings in one blade are in line with uncut portions of the second blade to prevent excitation emission from gaining access to the spectrograph or photometer. This allows a sample on the optical axis between the rotating blades to be illuminated (excited to phosphorescence), followed by a period of darkness, during which time its phosphorescence is allowed to pass the second disk and thence to the spectrograph or photometer.

The resolution time of such an arrangement

is the length of time between the cutoff of excitation to the sample and the clearing of the optical path by the second blade to allow the phosphorescent emission to pass. This time is a function of the motor speed, size and spacing of the cuts in the disks, relative radial position of the disks to each other, and the size of the slits.

The phosphoroscope serves two functions: (1) it allows the study of the phosphorescence free from any excitation emission and (2) it affords a unique way of resolving simple mixtures of phosphorescences based on their mean lifetimes. For example, if two compounds of different phosphorescence lifetimes are present in a mixture, the proper choice of disks and motor speeds may give a resolution time which will permit the shorter-lived compound to decay to a degree too weak to be detected, and the only measurable emission would be from the longer lived component.

In another case where the two lifetimes are nearly equal, resolution may possibly be gained by a spectroscopic resolution of the phosphorescent emission or by a selection of excitation frequency that will excite one phosphor and not the other. In a more difficult case where one phosphorescence cannot be completely isolated, relative intensity values of two sets of conditions—one set optimum for one compound and the second set optimum for the other—may be determined and the concentration found through the solution of two simultaneous equations from appropriate experimental data.

RUSSELL J. KEIRS

GAMMA-RAY SPECTROMETRY

BASIC PRINCIPLES AND INSTRUMENTATION

Gamma spectrometry is the technique by which the intensities of the various gamma energies emanating from a radioactive source are measured. The technique can be used for qualitative identification of the components of radionuclide mixtures, and for quantitative determination of their relative abundance. Thus it is extremely valuable in any situation where mixtures of radioisotopes are present. Such situations arise in neutron activation analysis, analysis of nuclear fuel processing streams, analysis of corrosion products in nuclear reactors, and the like.

Most gamma spectrometers employ a scintillation detector, usually sodium iodide (thallium-activated) coupled to a photomultiplier tube. The output from this detector is in the form of electrical pulses the height of which is proportional to the amount of energy transferred by an incident gamma ray to the sodium iodide crystal. The accompanying instrumentation can be divided into two general types: single-channel and multi-channel pulse height analyzers. The single-channel instruments utilize two discriminators to form a "window" through which pulses of a narrow energy range pass. By continuously varying the base line of the "window" the entire spectrum is scanned. In the multi-channel analyzers the spectrum is divided into as many parts as there are channels and the number of pulses falling into each channel are recorded simultaneously.

The multi-channel analyzers thus enable one to obtain much better precision in the same over-all time than is possible with single-channel equipment and have many advantages when short-lived nuclides are being measured. However, it should be noted that these instruments are quite expensive and generally require considerable maintenance.

A good single-channel instrument incorporating excellent stability and linearity of response can be purchased for a few thousand dollars and is quite satisfactory for most operations.

Frequently problems arise in resolving the spectra emitted by radionuclide mixtures because of overlapping of photopeaks. Also, depending on the size of the crystal used as a detector, the low-energy radiation produced by Compton scattering of high-energy photons may be a serious interference. In some cases these interferences may be removed merely by allowing radioactive decay to take place. More often, however, it is necessary to perform radiochemical separations. Procedures for such separations have been worked out for most elements and a number of compilations are available.¹ Nearly all of these use a known amount of a non-radioactive isotope as a carrier for the element being separated. These procedures can usually be adapted with only slight modifications to any system under study. Where several elements must be separated from the same sample the procedure becomes somewhat more complex, but usually a satisfactory separation scheme can be adapted from the standard outline for qualitative analysis.² Note that the carrier technique makes it possible to utilize separations which are rapid and specific although they may not be completely quantitative.

In theory it is possible to calculate absolute disintegration rates from gamma spectra knowing the detector efficiency, the geometry, and the radioactive decay scheme of the isotope being measured. In actual practice, however, the desired accuracy can be obtained much more readily by comparison to a standard. This is particularly true in neutron activation analysis where irradiation of a standard together with the unknown eliminates the need for accurate knowledge of

neutron flux and absorption cross-section in addition to the factors listed above.

In the companion article on Neutron Activation Products Analysis (Clark) there is tabulated the list of chemical elements analyzable by neutron activation, the radioisotope formed, the half-life, the experimental sensitivity in parts per million and the major x-ray peak or peaks in m.e.v. units.¹

REFERENCES

1. KLEINBERG, J., LA-1721 (Rev.) 1956.
2. See, for example, THOMPSON, B. A., *et al.*, *Anal. Chem.*, **30**, 1023 (1958).
3. GUINN, V. P., AND WAGNER, C. O., *Anal. Chem.*, **32**, 317 (1960).

BARBARA A. THOMPSON

MINIATURE SCINTILLATION SPECTROMETER

To measure the uranium-235 content of nuclear fuel elements, in accordance with AEC regulations for a 4% use charge, a low-cost transistorized spectrometer weighing less than 50 pounds has been developed by F. K. White.

In counting γ -rays given off by U^{235} , the device tells, in three to five minutes, how much isotope is present. Accuracy is to within ± 0.5 to 1%. Two things help bring this about. With the detector system consisting of sodium iodide crystal, photomultiplier tube, and preamplifier, AEC uses a small "Lucite" shield to absorb β -radiation. It also puts water coils around the photomultiplier tube to control temperature. Temperature changes in the tube throw off the results.

If U^{235} is not equally distributed through an element, the element may be scanned to get an average counting rate over its length.

The operator puts a standard of known weight and uranium content before the detector, then the unknown. The standard should have about the same count rate as the unknown. A lead collimator keeps geometry constant. The analyst corrects for self-absorption and then sets up a proportion

that tells him how much U^{235} the unknown element contains.

Another method may be used which is better for mass production, when maybe every fifth fuel element must be checked. Here the analyst uses three knowns, determined chemically. The second one has a higher count rate than the first, the third higher than the second. Next he plots the count rates of the knowns against their U^{235} contents, which give a linear curve over a limited range. After the operator finds the count rate of the unknown, he uses the curve to find the amount of U^{235} in the unknown. Thus, a standard need not be found for each test.

G. L. CLARK

MÖSSBAUER RADIATION

In 1958 Rudolph L. Mössbauer¹ announced discovery of a new effect in the emission and absorption process for low-energy γ -rays. Since September 1959 this effect, designated as Mössbauer radiation, has been confirmed in other laboratories. Most significant is the fact that the γ -radiation involved has a frequency which is more stable by many orders of magnitude than the best atomic clocks available today (see articles under Microwave Spectroscopy). For a detector, an absorber is employed which is similar to the radiator in that its absorption effect exists over the extremely small frequency range of the radiator. The experimental technique is explained by Kock² in a splendid review article.

When the radiator is stationary relative to the absorber, the frequency of the radiated γ -ray and that of the absorber are identical and the counter reads a relatively low value. If, now, the radiator is set in motion relative to the absorber, a Doppler shift is imparted to the radiated electromagnetic wave and the two frequencies differ. The "stop band" of the absorber "filter" is no longer effective

at the Doppler shifted frequency, and the counter reads a higher value than before.

From the velocity of the radiator as measured experimentally, the amount of Doppler frequency shift is known, and the frequency characteristics of the source and absorber can be ascertained. The measured line half-width of the γ -ray of the isotope of iron-57, as measured by R. V. Pound and G. A. Rebka, Jr., of Harvard University,³ corresponds to a source velocity of 0.017 cm/sec. When one considers that the velocity of light is 3×10^{10} cm/sec, the remarkable frequency stability of the γ -ray is evident. A velocity of one million millionth that of light has shifted the radiating frequency an appreciable amount from the absorber "filter" band. The center frequency of the line is 10^{13} times the line width; if a regulation capability of one thousandth of the line width (the capability normally achieved in present atomic clocks) is assumed, "the 'least count' in the Pound and Rebka experiment is about 3 parts in 10^{16} ".³

It is immediately apparent that this discovery has provided the experimental physicist with a new and powerful tool. At Harvard³ and at Harwell, England⁴ proof already has been obtained on the gravitational red shift predicted by relativity theory, according to which a clock 2000 miles above the earth would differ from an identical clock on earth by 1 second in 500 years. However only a slight difference in height is needed at constant temperature for shifting the frequency of one device relative to the other in the Mössbauer effect.

Points of great interest are how such a narrow line of radiation can occur, and why it has not been observed before. The γ -rays under consideration are emitted by nuclei, and normally the nucleus would experience a recoil upon emission of the γ -ray, thereby causing the frequency of the ray to be shifted by various amounts.

Mössbauer considered the possibility that a nucleus held by the strong binding forces

in a crystal lattice might cause the entire crystal lattice to absorb the recoil, and that this sharing of the recoil among huge numbers of atoms would permit the observed line width to be limited only by the length of the wave train, for example, of an iron-57 photon which has roughly 10^{12} waves, its frequency being 3×10^{18} cycles per second and its half-life 10^{-7} second. From the uncertainty relation $\Delta\gamma\Delta t \approx 1$, one arrives at the half-line width of 1 part in 10^{12} . The crystal recoil effect is also present in the absorber; its nuclei are accordingly in exact resonance with the unshifted line from the source.

REFERENCES

1. MÖSSBAUER, R. L., *Z. Physik*, **151**, 124 (1958).
2. KOCK, W. E., *Science*, **131**, 1588 (1960).
3. POUND, R. V., AND REBKA, G. A., JR., *Phys. Rev. Letters*, **3**, 439, 554 (1959); **4**, 337 (1960).
4. CRANSHAW, T. E., SCHIFFER, J. P., AND WHITEHEAD, A. B., *Phys. Rev. Letters*, **4**, 163 (1960).

G. L. CLARK

NEUTRON ACTIVATION PRODUCTS ANALYSIS

The most rapidly progressing technique of chemical analysis for extremely minute traces to ppb (parts per billion) of chemical elements employs a beam of neutrons for activation of isotopes which can then be identified, with counters, by the radioactive characteristics of the new nuclear species. Conventional analysis employs activation, followed by addition of carriers and hold-back carriers, and then by regular wet chemical separations before counting. While extremely sensitive, the chemical operations are time-consuming and the time delay precludes the utilization of many short-lived activities developed in the sample. This is avoided in many cases by a direct instrumental approach involving rapid identification by β -ray energy and half-life, or by γ -ray spectrometry. An excellent typical example of the method routinely used in an industrial laboratory is described by Guinn and Wag-

ner.⁴ The basic equation of activity, A_0 , in disintegrations per second at zero decay time, generated per gram of element by exposure to a thermal neutron flux, f , (neutrons $\text{sec}^{-1} \text{cm}^{-2}$) for a period of time t_i is

$$A_0 = Nf\sigma \left(1 - \exp \frac{-0.693 t_i}{t_{0.5}} \right)$$

where N is the number of target nuclei per gram of element, capable of forming the radioisotope in question by the (n, γ) reac-

TABLE 1

Element	Radioisotope Formed	Half-Life	PPM Exptl.	Major γ -Peaks m.e.v.
Na	Na ²⁴	15h	6.4	1.37, 2.75
Mg	Mg ²⁷	9.5m	82	0.84
Al	Al ²⁸	2.3m	2.4	1.78
Cl	Cl ³⁸	37m	6.8	1.59, 2.16
K	K ⁴²	12.5h	150	1.53
Ca	Ca ⁴⁸	8.7m	270	3.10
Ti	Ti ⁵¹	5.8m	40	0.32
V	V ⁵²	3.8i	0.20	1.44
Cr	Cr ⁵¹	27d	1300	0.32
Mn	Mn ⁵⁶	2.6d	0.12	0.84
Co	Co ^{60m}	10.5m	0.45	0.059
Ni	Ni ⁶⁵	2.6h	320	0.39, 1.10, 1.49
Cu	Cu ⁶⁴	13h	4	0.51
	Cu ⁶⁶	5.1m		1.04
Zn	Zn ^{69m}	14h	370	0.44
As	As ⁷⁶	27h	5.2	0.56
Br	Br ⁸⁰	18m	1.4	0.51, 0.62
	Br ⁸²	36h		0.55-0.83
Mo	Mo ¹⁰¹	15m	14	0.19
	Tc ¹⁰¹	15m		0.30
Ru	Ru ¹⁰⁶	4.5h	38	0.73
	Rh ¹⁰⁶	37h		0.32
Ag	Ag ¹⁰⁸	2.3m	1.2	0.63
In	In ¹¹⁶	54m	0.081	0.41, 1.09, 1.27
Sn	Sn ¹²³	40m	40	0.15
	Sn ¹²⁶	9.5m		0.33
Sb	Sb ^{123m}	3.5m	8.9	0.061, 0.075
	Sb ¹²²			0.56
I	I ¹²⁸	25m	1.0	0.45
Re	Re ^{188m}	20m	0.5	0.06
	Re ¹⁸⁸	17h		0.16
W	W ¹⁸⁷	24h	3.5	0.07, 0.13, 0.48-0.69
Pt	Pt ¹⁹⁹	30m	17	0.074, 0.020, 0.54
Au	Au ¹⁹⁹	3.1d		
	Au ¹⁹⁸	2.7d	1.3	0.41

tion; σ is the isotopic thermal neutron capture cross section, in square centimeters per nucleus (tabulated in reference 6); and $t_{0.5}$ is the half-life of the radioisotope formed. The irradiation time is also a very useful parameter for simplification of the γ -ray spectrum produced by a complex sample; brief irradiation, followed by rapid counting, produces a spectrum in which the short-lived activities predominate, while a longer time of irradiation followed by a long decay time before counting accentuates the longer-lived activities. In the work referred to above, the neutron flux of 10^8 is provided by bombardment of a beryllium block with 3 mev electrons ($\text{Be}^9(x, n) \rightarrow 2\text{He}^4$). The γ -ray spectra are obtained by amplifying the output of a scintillation counter and feeding the amplified pulses to a 100-channel pulse height analyzer. Rapid and successful analyses are made of polymers for chlorine, organic ethers for bromine, petroleum, cracking catalysts for Al and Mg, reforming catalysts for Al, Pt and Cl, dehydrodesulfurization catalysts, inhibited sulfuric acid for Na, As, and Mn. Other recently reported analyses are for silicon carbide,⁵ aluminum-base alloys,¹ arsenic in reforming catalysts,⁷ halides in ZnS phosphors,² and trace impurities in tungsten.³ For convenience, Table 1, from the work of Guinn and Wagner, presents the list of chemical elements analyzable by neutron activation, the radioisotope formed, the half-life in minutes (m), hours (h) or days (d), the experimental sensitivity (which in some cases varies from theoretical) in parts per million and the major γ -spectrum peak in mev units.

REFERENCES

1. BROOKSBANK, W. A., LEDDICOTTE, G. W., AND DEAN, J. A., *Anal. Chem.*, **30**, 1785 (1958).
2. COSGROVE, J. F., BASTIAN, R. P., AND MORRISON, G. H., *Anal. Chem.*, **30**, 1872 (1958).
3. COSGROVE, J. F., AND MORRISON, G. H., *Anal. Chem.*, **29**, 1017 (1957).
4. GUINN, V. P., AND WAGNER, C. O., *Anal. Chem.*, **32**, 317 (1960).

5. LOWE, L. F., THOMPSON, H. D., AND CALI, J. P., *Anal. Chem.*, **31**, 1957 (1959).
6. MEINER, W. W., AND MADDOCK, R. A., *Anal. Chem.*, **29**, 1171 (1957).
7. SHIPMAN, G. F., AND MILNER, O. I., *Anal. Chem.*, **30**, 210 (1958).

G. L. CLARK

PARTICLE SIZE ANALYSIS BY γ -RAY ABSORPTIOMETRY*

An interesting application of γ -ray or X-ray absorptiometry is the rapid size analysis of sub-sieve particles. In sedimentation methods of size analysis, the laborious procedure of sampling the suspension at various times can be replaced by a continuous measurement based on the attenuation of γ -rays or X-rays from a monoenergetic source. As particles settle from a uniform suspension, their concentration at a fixed depth is determined by measuring the transmittance of the suspension. A scintillation crystal, connected through a photomultiplier circuit to a count rate meter and recorder, can be used to measure the intensity of the emerging

beam. For particles of a given composition, the absorption depends only on the mass of the particles in the beam. Hence the settling rate curve can be converted directly to a standard curve of fraction undersize versus Stokes' law diameter.

A source of americium-241 provides a γ -beam that is especially suitable for analyzing particles of heavy metals or heavy metal compounds. Uranium oxide particles 5 to 50 microns in diameter at initial concentrations of 8 to 20 grams per liter of water were analyzed with this source.¹

Lighter particles (fly ash, iron oxide, bismuth oxide) from 7 to 76 microns in diameter and in concentrations of 2 to 3 grams per liter have been analyzed by means of X-ray absorption.²

REFERENCES

1. ROSS, C. P., "Particle Size Analysis by Gamma Ray Absorption," *Anal. Chem.*, **31**, 337-9 (1959).
2. BROWN, J. F., AND SKREBOWSKI, J. K., *Brit. J. Appl. Phys. Suppl.*, No. 3, S27-8 (1954).

C. P. ROSS

INFRARED EMISSION SPECTROSCOPY

The nature of the radiation emitted by a hot body is one of the classic problems of physics. The correct explanation of black-body emission in the celebrated Planck radiation law is a triumph of modern physics and forms the cornerstone of quantum mechanics. Early in the history of infrared spectroscopy emission spectra were studied as enthusiastically as absorption spectra. Later investigators neglected emission studies, partly because of the challenge presented by the spectacular fine structure to be resolved

and explained in absorption spectra, and perhaps partly because obtaining a meaningful emission spectrum requires accurate intensity measurements, which are very difficult.

In recent years, a new interest has grown in thermal emission phenomena. To a great extent the reasons for this interest are found in the need for data by the designers and analysts of military devices involving heat transfer. As an example, high speed aircraft and missiles become very hot by frictional heating and it is desirable to cover their surfaces with a highly emissive coating to aid in cooling.

* Information developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

INFRARED EMISSION SPECTROSCOPY

The standard emitter of thermal radiation is the ideal black body which, by definition, absorbs all radiant energy falling on it. The power radiated from unit area of a black body at temperature T in the wavelength interval between λ and $\lambda + d\lambda$ is given by Planck's equation

$$J(\lambda, T) d\lambda = \frac{c_1}{\lambda^5 (e^{c_2/\lambda T} - 1)} d\lambda \quad \text{(Planck radiation law)}$$

with $c_1 = 3.740 \times 10^{-12}$ watt-cm², $c_2 = 1.438$ cm degrees; λ and T are in centimeters and degrees Kelvin, respectively. This equation is closely approximated by the older equations of Wien and of Rayleigh and Jeans for sufficiently low and high values, respectively, of λT :

$$J(\lambda, T) d\lambda = \frac{c_1}{\lambda^5} e^{-c_2/\lambda T} d\lambda \quad \text{(Wien radiation law)}$$

$$J(\lambda, T) d\lambda = \frac{c_1 T}{c_2 \lambda^4} d\lambda \quad \text{(Rayleigh-Jeans radiation law)}$$

The total power radiated per unit area by a black body is given by the Stefan-Boltzmann law

$$J(T) = \sigma T^4, \quad \sigma = 5.669 \times 10^{-12} \text{ watt/cm}^2 \text{ degree}^4 \quad \text{(Stefan-Boltzmann law)}$$

which can be obtained from the Planck law but which was derived from thermodynamics much earlier. The spectral distribution of radiation from a black body has a maximum at a wavelength λ_m the temperature dependence of which is described by the Wien displacement law

$$\lambda_m T = \text{constant} \quad \text{(Wien displacement law)}$$

The value of the constant depends on the way in which the spectral radiation density is defined. Its value is 0.2897 cm degree for maximum radiation per unit *wavelength* interval and 0.5098 cm degree for unit *frequency* interval.

The radiant power emitted per unit area

by an ideal black body at a given wavelength can be approached but never surpassed by a real body at the same temperature. The emittance of a body at a given wavelength is defined as the ratio of the power emitted per unit area of the body to the power emitted per unit area by a black body at the same temperature. In general, the emittance can vary with temperature as well as with wavelength. The characteristics of an ideal black body can be closely approximated by an artificial black body which usually takes the form of an enclosure (hohlraum) with a small opening through which radiation is sampled. The extent of departure from ideality of such a body can be calculated in terms of its geometry, relative size of the opening, and the reflectivity of the wall material. Carbon is a convenient construction material, has high emittance, and can be heated electrically.

The relationship between emission, absorption, and reflection is given by Kirchoff's law which states that the emittance of a body is equal to the absorptance, i.e. the fraction of incident radiation absorbed by the body. But absorptance can be defined in terms of transmittance and reflectance. Hence, the emittance of an opaque substance can be determined from its reflectance. An important consequence of Kirchoff's law is that the emittance of a specimen which is not opaque depends on its transmittance and therefore on its thickness. Lambert's cosine law states that the energy emitted per unit solid angle from a plane surface is proportional to the cosine of the angle between the direction of emission and the normal to the surface. This is a geometrically derived expression which is true for most materials for angles not too large, but at large angles deviations occur, in part because the reflectance of surfaces becomes great for large angles of incidence. The surface condition of a specimen also plays an important role in determining its emittance, largely through the effect on reflectance.

There are a number of approaches to the measurement of infrared emission spectra. Perhaps the most direct method is to place the specimen, with its heating apparatus, in a single beam spectrometer in place of the usual source and record the signal obtained as wavelength is scanned. The record obtained will not be the true emission spectrum of the sample because of the influence of the spectrometer itself, due to such factors as variation in spectral band width with dispersion, absorption by the prism and by atmospheric water vapor and carbon dioxide, optical aberrations, and variations in detector sensitivity, all of which are dependent on the wavelength. These effects can be eliminated and at the same time a true *emittance* spectrum obtained by recording the emission from a black body under the same instrumental conditions and plotting the ratio of the signals obtained for the sample and for the black body as a function of wavelength.

The advantages of double beam spectroscopy can be exploited, in principle, by placing the specimen in the sample beam and a black body in the reference beam of a double beam instrument and recording the emittance spectrum directly, with instrument and atmospheric effects automatically canceled from the spectrum. There are practical complications in the double beam approach because of the necessity for adjusting the sample and reference beams for equal transmission. This can be done, for example, by mounting a black body in each beam. A compromise between the single- and double-beam methods employs a double-beam instrument in which first the emission from the specimen and then the emission from the black body are recorded relative to the usual spectrometer source. These records will be free from the sharp absorption lines of atmospheric water vapor and their ratio will be more easily plotted than in the true single beam method despite severe demands made on the stability of the source.

An indirect method for the determination

of the emittance of a specimen which is *known to be opaque* is to measure the reflectance of the heated specimen from which its emittance can be deduced using Kirchhoff's law, $\text{emittance} = 1 - \text{reflectance}$. It is necessary to differentiate between reflected and emitted radiation from the sample. This can be done by recording spectra with and without the spectrometer source or by utilizing an instrument with a radiation chopper located between the source and the specimen, so the emitted radiation will not be modulated and therefore not detected. In principle, the reflectance method can be used for transmitting samples as well as opaque ones, provided the transmittance can be determined. In this case $\text{emittance} = 1 - \text{apparent transmittance} - \text{apparent reflectance}$. The apparent transmittance is less than the true transmittance and the apparent reflectance is greater than the true reflectance because of internal reflections within the specimen.

Solid specimens are usually heated either electrically or with a flame. Conducting or semi-conducting materials can be electrically heated by direct conduction. Non-conductors can often be coated on conducting metal strips and heated by contact with the hot metal, although in the case of non-opaque specimens the effect of radiation from the metal surface must be considered. Materials which will not adhere to large heated surfaces can sometimes be applied to fine metallic screens and heated electrically. Flames can be used to heat specimens of various forms either directly or indirectly. Emission from the flame itself must be taken into consideration if it can be intercepted by the spectrometer. Fine metallic or ceramic screens can also be heated by a flame, but it is often convenient to coat a combustible fabric with the specimen. The supporting material is then burned away leaving a fine delicate mesh of the specimen itself. The Welsbach mantle is made in this way, with thorium oxide as the emitting material. Induction

heating in radio-frequency fields, heating by solar or other high intensity radiation, and heating in a plasma jet are also potentially useful methods for the production of emission spectra. Emission studies are not restricted to high temperatures. Modern engineering often requires data for calculating radiant heat transfer between cold objects, for example between artificial satellites and the sky. Laboratory measurements of low temperature emittance are made with refrigerated samples and reference bodies, care being taken that objects in the optical system, such as warm choppers, do not interfere.

The foregoing discussion has been phrased in terms of emission from solid bodies. Gaseous samples also provide meaningful infrared emission spectra, however of a somewhat different nature. The thermal emission spectra of solid bodies are derived largely from the thermal motion of electrons modified by the vibrations of molecules and crystal lattices, if any, and usually are somewhat structureless with broad, undetailed bands. On the other hand, emission from gases in the infrared arises mostly from the transitions between vibrational and rotational energy states. Hence emission spectra of thin layers of gas consist of narrow lines separated by regions of relatively low emittance. For sufficiently thick layers of gas the transmittance vanishes even at wavelengths of rather weak absorptivity. Since the reflectance of a gas is negligible, Kirchhoff's law tells us that thick layers of gas emit as black bodies, and indeed our sun is a black body.

Applications of infrared emission spectroscopy of gases can be divided into two general categories. One is concerned with qualitative identification of species existing in reaction systems, such as flames or electrical discharges, in much the same way as absorption spectroscopy is used. Sometimes rapid scanning spectrometers are used to follow the course of fast reactions. The other application is the measurement of the temperature

of gaseous systems too hot for ordinary thermometry. Most temperature measurements are based on one of two general principles, each of which can be applied in a number of ways. The first approach is to use the radiation laws and a comparison black body. As one example of many such techniques, in the "reversal" method, radiation from a black body is allowed to pass through the hot gas and is then chopped and focused on the spectrometer. From Kirchhoff's law, if the temperature of the black body is adjusted to equal the temperature of the gas, the absorption by the gas will be just balanced by its emission and neither absorption nor emission lines will be observed. The other general approach to temperature measurement of hot gases makes use of the proportionality between the number of molecules in a given energy state and the Boltzmann factor, $e^{-E_n/kT}$, where E_n is the energy of the state, k is Planck's constant, and T is the absolute temperature. The intensity of an emission line is proportional to, among other things, the number of molecules in the energy state responsible. Therefore, if a spectrum can be analyzed in sufficient detail to correlate its lines with the rotational or vibrational states of the molecule it is theoretically possible to determine the temperature from a measurement of the intensities of some of the emission lines. In practice there are many difficulties associated with these measurements. To name a few, the effects of self absorption must be accounted for; quite high resolution is required to obtain meaningful intensities of narrow rotational lines; other factors in the expression for emission line intensities need to be determined; and finally, if the gas does not constitute an equilibrium system the concept of "temperature" becomes ambiguous and different values may be obtained depending on the system of emission lines measured.

Infrared emission from hot liquids has received even less attention than solids and

gases. Emission spectra of liquids can be observed by heating a thin film between transparent windows. Emission from liquid films originates in the molecular vibrational transitions and the spectra are intermediate in character between the broad features of solid spectra and the sharp lines of gases. The emission of a thick liquid layer approaches that of a black body, just as in the case of gases.

REFERENCES

- RUTGERS, G. A. W., "Temperature Radiation of Solids," *Handbuch der Physik*, XXVI, pp. 129-170, Springer-Verlag, Berlin (1958).
- WORTHING, A. G., "Temperature Radiation Emissivities and Emittances," "Temperature, Its Measurement and Control in Science and Industry," pp. 1164-1187, Reinhold Publishing Corp., New York (1941).
- McMAHON, H. O., "Thermal Radiation from Partially Transparent Reflecting Bodies," *J. Opt. Soc. Am.*, **40**, 376 (1950).
- GORDON, R., "The Emissivity of Transparent Materials," *J. Am. Ceram. Soc.*, **39**, 278 (1956).
- DIEKE, G. H., "High Gas Temperatures," "Temperature, Its Measurement and Control in Science and Industry," Volume 2, pp. 19-30, Reinhold Publishing Corp., New York, 1955.
- BROIDA, H. P., "Experimental Temperature Measurements in Flames and Hot Gases," *Ibid.*, pp. 265-286.
- KAPFF, S. F., "Infrared Emission Spectra of Hot Liquids," *J. Chem. Phys.*, **16**, 446 (1948); *Science*, **104**, 274 (1946).
- PENNER, S. S., "Quantitative Molecular Spectroscopy and Gas Emissivities," Addison-Wesley Publishing Co., Reading, Mass, 1959.

JAMES E. STEWART

INFRARED SPECTROPHOTOMETRY

AMINES (PRIMARY AROMATIC) STRUCTURES

As part of their pioneering work dealing with the near-infrared spectral region, Wulf and Liddel^{1, 2} investigated the first overtone N—H bands of several primary amines. Instrumental limitations prevented them from studying the combination N—H bands, which occur near 2 microns. These near-infrared bands received little further attention until recently, when the overtone and combination N—H bands of aniline and 39 of its ring-substituted derivatives were investigated.³ This study resulted in the development of several relations between the positions and the intensities of the N—H bands and the structures of the amines. A discussion of these spectra-structure relations follows.

The compounds which were studied are listed in Table 1. Data on the positions and the intensities of the overtone and combination N—H bands of the compounds are

summarized in Table 2. The data were obtained with carbon tetrachloride solutions containing 1 % or less of the amines (0.1 *M* or less).

Frequency-Structure Relations. Compounds with strong electron-withdrawing substituents fall at the upper ends of the frequency ranges shown in Table 2 and those with strong electron-donating substituents fall at the lower ends. For a given band of meta- and para-substituted compounds, two linear relations exist between frequency and the values of Hammett's substituent constants, σ or σ_p^* . One relation holds for negative values of σ (electron-donating groups), and another of considerably smaller slope holds for positive values of σ . By using a combination of Brown's σ^+ values and Hammett's σ (or σ_p^*) values, however, a single linear relation fits the data for all meta- and para-substituted compounds. This relation for the first overtone symmetric

INFRARED SPECTROPHOTOMETRY

TABLE 1. RING-SUBSTITUTED ANILINES

Meta- and Para-Substituted Compounds		Ortho-Substituted Compounds	
Compound No.	Substituent	Compound No.	Substituent
1	<i>p</i> -N(C ₂ H ₅) ₂	25	<i>o</i> -SCH ₃ ^b
2	<i>p</i> -NH ₂	26	2-CH ₃ -4-N(C ₂ H ₅) ₂
3	<i>p</i> -OC ₂ H ₅	27	<i>o</i> -OC ₂ H ₅
4	<i>p</i> -OCH ₃	28	2,5-(OC ₂ H ₅ - <i>n</i>) ₂
5	<i>p</i> -CH ₃	29	2,5-(OC ₂ H ₅) ₂
6	<i>p</i> -SCH ₃ ^a	30	<i>o</i> -OCH ₃
7	<i>p</i> -CH ₂ CH ₂ OH	31	2,5-(OCH ₃) ₂ -4-Cl
8	None	32	2,5-(OCH ₃) ₂
9	<i>m</i> -CH ₃	33	2,4,6-Cl ₃
10	<i>p</i> -C ₆ H ₅	34	<i>o</i> -SO ₂ CH ₃
11	3,5-(CH ₃) ₂	35	<i>o</i> -Br
12	<i>p</i> -Cl	36	<i>o</i> -CH ₃
13	<i>m</i> -OC ₂ H ₅	37	2,4,5-Cl ₃
14	<i>m</i> -Br	38	2,4-Cl ₂
15	<i>m</i> -COCH ₃	39	<i>o</i> -Cl
16	<i>m</i> -Cl	40	<i>o</i> -NO ₂
17	<i>p</i> -SCN		
18	<i>m</i> -CF ₃		
19	<i>m</i> -NO ₂		
20	<i>p</i> -COCH ₃		
21	<i>p</i> -SO ₂ CH ₃		
22	<i>p</i> -COOH		
23	<i>p</i> -CN		
24	<i>p</i> -NO ₂		

^a Purity of this compound only 92%.

^b Purity of this compound only 87%.

stretching band is shown in Figure 1. Equations 1-4 in Table 3 describe this line and similar ones obtained for the other bands.

Attempts to relate the frequencies of ortho-substituted anilines with Taft's σ_{ortho} constants, or with the sum of these values and Brown's σ^+ values in cases of multiple substitution, were unsuccessful.

Frequency-Frequency Relations. The frequencies of the various N-H bands of meta- and para-substituted anilines are linearly related. The relation between the symmetric and the asymmetric first overtone bands is shown in Figure 2. Equations 5-8 in Table 3 describe this relation and similar ones for other pairs of bands.

The relations found between various pairs of frequencies for meta- and para-substituted compounds are valid for compounds having a methyl group ortho to the amino group, but not for those having other ortho substituents. For example, the first overtone asymmetric frequencies of ortho-substituted anilines are 10 to 20 cm⁻¹ higher, with respect to the symmetric frequencies, than those of meta- and para-substituted compounds (Figure 2). Similarly, the overtone stretching frequencies are high with respect to the combination frequencies, and the second overtone frequencies. In the case of the first overtone asymmetric and combination frequencies, a reasonably good linear relation also exists for the ortho-substituted compounds (equation 9, Table 3).

Intensity-Structure and Intensity-Frequency Relations. The molar absorptivities of the first overtone symmetric bands vary from 1.15 to 1.76, the majority of the values falling between 1.21 and 1.35. Substitution of any type, with the exception of *o*-bromo and *m*-ethoxy groups, results in stronger absorption relative to that of aniline. This effect is most pronounced with 4-biphenylamine, polychlorinated anilines, and compounds with strong electron-attracting groups in the meta or para position.

The first overtone asymmetric stretching band of aniline has a molar absorptivity of 0.16. Electron-donating substituents in the meta or para position have little effect on the intensity of this band. Electron-withdrawing substituents, however, increase the intensity sharply, the relation between intensity and σ being approximately linear (equation 10, Table 3). *o*-Alkoxy substituents weaken the asymmetric band, but *o*-halo, *o*-methylsulfonyl, and *o*-nitro substituents strengthen the band considerably.

The intensity of the combination band is linearly related to the electronic nature of meta and para substituents, as described by equation 11 in Table 3. Since both the frequency and the intensity increase linearly

AMINES (PRIMARY AROMATIC) STRUCTURES

TABLE 2. POSITIONS AND INTENSITIES OF THE OVERTONE AND COMBINATION N—H BANDS OF RING-SUBSTITUTED ANILINES

	Combination	1 st Overtone Symmetric	1 st Overtone Asymmetric	2 nd Overtone Symmetric
Frequency, cm. ⁻¹				
Range	5104-5045	6791-6609	6982-6850	9970-9662
Average	5071.5	6701.9	6913.4	9810.6
Std. Dev.	16.0	21.2	31.7	34.8
Wave Length, m μ				
Range	1959-1982	1472-1513	1432-1460	1003-1035
Average	1971.9	1492.2	1446.5	1019.3
Std. Dev.	6.2	4.7	6.7	3.7
Molar Absorptivity*				
Range	1.23-2.65	1.15-1.76	0.13-0.43	0.026-0.047
Average	1.75	1.35	0.204	0.036
Std. Dev.	0.37	0.14	0.075	0.006

* Units are liter/mole-cm.; dilute solutions in carbon tetrachloride; background absorbances at 1915, 1575, 1410-1420, and 1075 m μ were subtracted from the peak absorbances of the combination, first overtone symmetric, first overtone asymmetric, and second overtone symmetric bands, respectively, before the absorptivities were calculated.

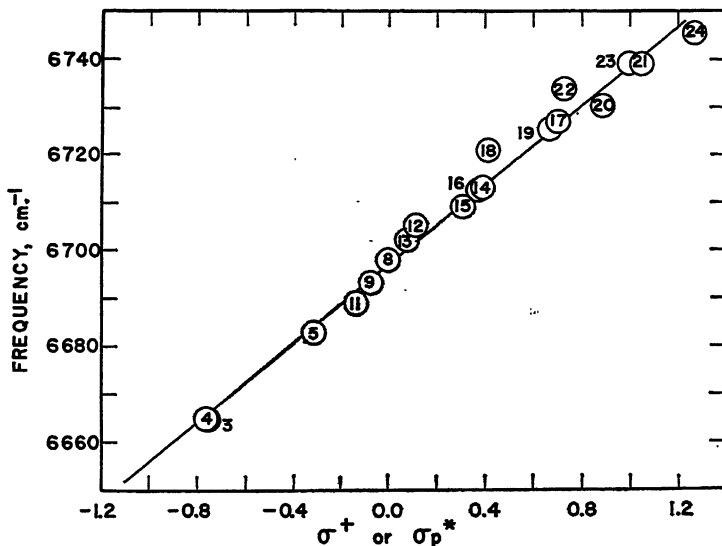


FIG. 1. First overtone N-H symmetric stretching frequency vs. Brown's σ^+ and Hammett's σ_p^* constants for *m*- and *p*-substituted anilines. (See Table 1)

with σ , the intensity of the combination band should also increase linearly with frequency. The bottom line in Figure 3 shows that this relation holds reasonably well for meta- and para-substituted anilines. Somewhat surprisingly, the intensity-frequency relation for ortho-substituted anilines is also

linear (top line, Figure 3), although the relation is not the same as the one for meta- and para-substituted compounds. Equations 12 and 13 in Table 3 describe the two lines in Figure 3.

Miscellaneous. The average ratio of absorptivities of the first and second overtone

INFRARED SPECTROPHOTOMETRY

TABLE 3. SPECTRA-STRUCTURE RELATIONS FOR THE N—H BANDS OF RING-SUBSTITUTED ANILINES

No.	Equation	Std. Dev. ^a	Correlation Coefficient	Substituents
1	$\nu_{1st}^{o.t. \text{ sym.}}, \text{ cm.}^{-1} = 41.3 \sigma^+ (\text{or } \sigma_p^*) + 6697.4$	2.9	0.992	<i>m, p</i>
2	$\nu_{1st}^{o.t. \text{ asym.}}, \text{ cm.}^{-1} = 52.2 \sigma^+ (\text{or } \sigma_p^*) + 6902.2$	3.1	0.994	<i>m, p</i>
3	$\nu_{comb.}, \text{ cm.}^{-1} = 24.8 \sigma^+ (\text{or } \sigma_p^*) + 5074.0$	2.6	0.985	<i>m, p</i>
4	$\nu_{2nd}^{o.t. \text{ sym.}}, \text{ cm.}^{-1} = 69.7 \sigma^+ (\text{or } \sigma_p^*) + 9802.2$	5.7	0.989	<i>m, p</i>
5	$\nu_{1st}^{o.t. \text{ sym.}} = 0.790 (\nu_{1st}^{o.t. \text{ asym.}} - 6911.0) + 6704.3$	3.2	0.993	<i>m, p</i>
6	$\nu_{1st}^{o.t. \text{ sym.}} = 1.58 (\nu_{comb.} - 5077.6) + 6704.3$	4.6	0.983	<i>m, p</i>
7	$\nu_{1st}^{o.t. \text{ asym.}} = 1.98 (\nu_{comb.} - 5077.6) + 6911.0$	6.7	0.984	<i>m, p</i>
8	$\nu_{2nd}^{o.t. \text{ sym.}} = 1.61 (\nu_{1st}^{o.t. \text{ sym.}} - 6699.6) + 9806.5$	5.7	0.990	<i>m, p</i>
9	$\nu_{1st}^{o.t. \text{ asym.}} = 2.10 (\nu_{comb.} - 5062.9) + 6925.8$	12.2	—	<i>o</i>
10	$\epsilon_{1st}^{o.t. \text{ asym.}} = 0.191 \sigma^+ (\text{or } \sigma_p^*) + 0.135$	0.03	—	<i>m, p</i>
11	$\epsilon_{comb.} = 0.372 \sigma^+ (\text{or } \sigma_p^*) + 1.61$	—	—	<i>m, p</i>
12	$\epsilon_{comb.} = 0.0134 (\nu_{comb.} - 5075.9) + 1.653$	0.11	—	<i>m, p</i>
13	$\epsilon_{comb.} = 0.0246 (\nu_{comb.} - 5063.0) + 1.950$	0.12	—	<i>o</i>

^a Expressed in cm.^{-1} for equations 1-9 and in molar absorptivity for equations 10-13.

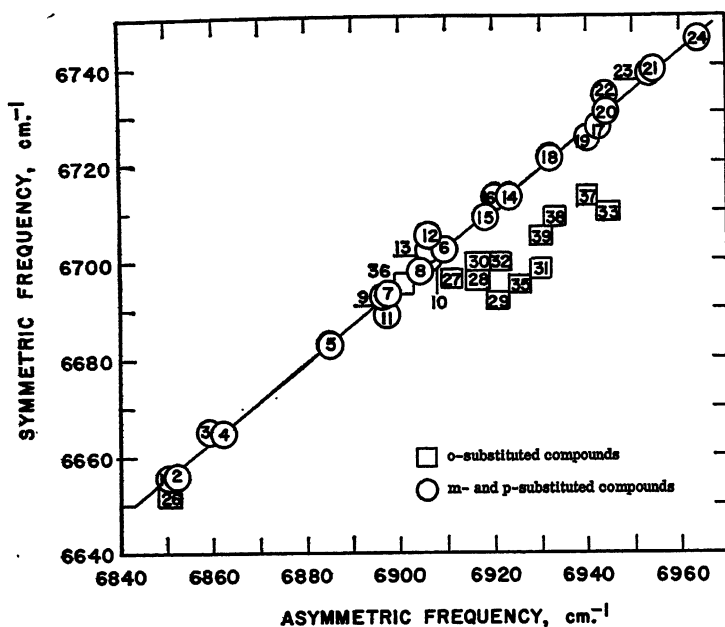


Fig. 2. Relations between first overtone N—H symmetric and asymmetric stretching frequencies of substituted anilines. (See Table 1)

symmetric bands is about 37:1, the individual values ranging from 29 to 52. Attempts to relate this ratio with structure were unsuccessful.

The first overtone symmetric bands of *o*-nitro-, *o*-methylsulfonyl-, and *o*-methylthioaniline are split into two components

which are of about equal intensity and are separated by $100 \pm 4 \text{ cm.}^{-1}$ ($23.5 \pm 1 \text{ m}\mu$). The high- and low-frequency bands are presumably due to free and intramolecularly bonded N—H groups, respectively.

Conclusion. These relations between spectra and structure can be used to ad-

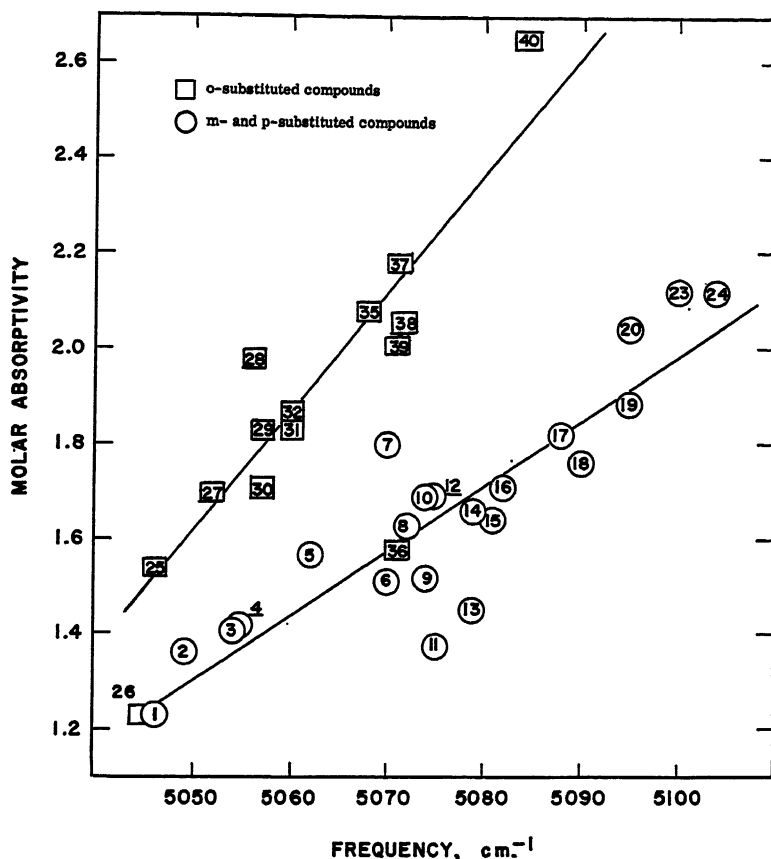


FIG. 3. Relations between intensity and frequency for the N-H combination bands of substituted anilines. (See Table 1)

vantage in identifying unknown aromatic amines. Having established by the presence of the combination N—H band near 1.97 microns that the compound is a primary amine, the relative positions of the overtone and combination bands show with reasonable certainty whether there is a substituent ortho to the amino group. Confirming evidence on this point can be obtained from the relation between the intensity and the frequency of the combination band. In the absence of ortho substitution, the positions of the bands provide considerable information on the electronic nature of the substituent. The intensities of the asymmetric stretching and combination bands can also be related to the type of substituent.

REFERENCES

1. LIDDEL, U., AND WULF, O. R., *J. Am. Chem. Soc.*, **55**, 3574 (1933).
2. WHETSEL, K. B., ROBERSON, W. E., AND KRELL, M. W., *Anal. Chem.*, **30**, 1598 (1958).
3. WULF, O. R., AND LIDDEL, U., *J. Am. Chem. Soc.*, **57**, 1464 (1935).

KERMIT B. WHETSEL

APPLICATIONS

Absorption

In discussion of the molecular model (cf. *Infrared Absorption*, Basis of, p. 450) the values of the characteristic absorption frequencies are dependent on three molecular characteristics: (1) the atoms, (2) the chemi-

cal bond forces, and (3) the spatial geometry. But these are the three fundamental characteristics used by the chemists to differentiate one molecular species from another. If two molecules have the three characteristics in common they are identical; if they differ in any characteristic, they are different. One would assume from this common basis for infrared absorption and species determination that the infrared absorption spectrum of a compound is likely to be unique to that compound. This proves to be true and from this uniqueness stems the three main uses of infrared in chemistry.

Material Characterization. The infrared spectrum of a molecule is the "most nearly unique" characteristic of that molecule. This results from the basis of the spectrum as discussed above. Even if such a close basis did not exist, the fact that a single criterion, the infrared spectrum, possesses 3N-6 (or more) values *distinct on the abscissa and the ordinate* provides a statistical probability of uniqueness that is unmatched by any other characteristic. For these reasons the infrared spectrum is often termed "the fingerprint of the molecule."

The use possibilities are tremendous—identification of an unknown by spectral matching with a known, tracing the course of distillation, chromatography, crystallization, establishing empirical limits of material acceptance, answering the simple question, "is it the same or different?"

For such purposes a library of pure spectra and references is desirable. Such compilations are available from references (1) and (2).

Qualitative Analysis for Functional Groups. Organic chemical compounds are, to a great extent, made up of various combinations of certain subgroups called functional groups, as hydroxyl, methyl, nitrile, carbonyl, etc. From the nature of infrared spectra, it is to be expected that such subgroups would have characteristic absorption regions by which their presence (or absence)

in an unknown might be determined. Considerable study has been made of this problem and published charts (Ref. 3) give a recent compilation of such data. Reference (4) offers more complete evaluation for hydrocarbons.

It can be seen that functional groups do have characteristic absorption in certain parts of the infrared spectrum and, in addition, variations in this range give some clue as to the relation of the group to the rest of the molecule.

Information of this type is very useful to the structural organic chemist in a study of unknown compounds since the infrared spectral evaluation may replace a variety of chemical spot tests. It must be used very carefully and considered in conjunction with all possible chemical data available.

Quantitative Analysis of Chemical Mixtures. Since the spectral characteristics of compounds are largely retained on admixture, the spectrum of a mixture is a superposition of the spectra of the individual components with allowance for the concentrations present. The method of analysis is to choose absorption frequencies unique to each component, measure the sample transmittance at the chosen frequencies, and relate the measurements to concentrations. This use of infrared probably represents the greatest volume application today.

Typical Analytical Problems. Alert chemists are continually adding to the wide range of problems for which infrared is becoming a routine analytical technique. With more than five thousand instruments in laboratories throughout the world, it is impossible to detail all its uses. But a look at what IR has done for a few typical companies and institutions may indicate what it can do for you.

A large manufacturer of cans has been using infrared for ten years to identify over 100 organic coatings in inventories, and to determine whether the coatings were properly cured. Film thicknesses of 0.04–0.6 mil make

classical techniques difficult, but with IR, film does not even have to be removed from the metal. With IR, too, the company identified the flavor components in fresh orange juice and the deterioration products in unrefrigerated canned juice; it is studying waxes, paper, sealing compounds and plastics.

An automobile manufacturer uses IR to study engine exhaust gases as a means of establishing relationships between vehicles and air pollution, determining the efficiency of combustion in engines, and evaluating devices to reduce or render harmless unburned hydrocarbons in exhaust fumes.

An electric power commission analyzes herbicides it buys for clearing rights-of-way. Its previous analysis for chlorine content could not distinguish between 2,4-D and 2,4,5-T, or prevent erroneous results arising from contamination with sodium chloride or other salts. IR gives exact concentration of each component in one-tenth the time required for chlorine analysis.

A cosmetic manufacturer, already using IR for raw material analysis, product control and formulation development, now checks jar caps and liners with IR as well, to guard against interaction with contents. A 10-20 minute spectrum run gives exact chemical composition of coatings instead of probable composition previously obtained by a complicated, time-consuming procedure.

An essential-oils house rates IR a good investment in speed and security since it establishes exact composition of complex natural perfumes impossible to analyze by other methods, and insures technical control in the manufacture of synthetic odorants and flavors.

A chemical producer who must keep water below 10 ppm in fluorochlorohydrocarbon refrigerant uses IR. With water present in the 0-10 ppm range, IR gives an accuracy of 1 ppm, and requires only 5 minutes. A previous analytical method required 4 hours, and was accurate only to 2 ppm.

An aircraft manufacturer used IR to learn when and why a polymeric coating kept breaking down at elevated temperatures. With IR, he was able to chart the chemical changes taking place in the coating at 25°C increments in temperature, and with these data, make a quick and meaningful evaluation of the finish problem.

A government health laboratory using IR has differentiated the various members of the barbiturate class of drugs, which, because of their structural similarity, can't be analyzed efficiently by other means.

A related project is the work of a United Nations unit in compiling IR spectra of confiscated narcotics according to the soil in which the material was grown. This will provide a library of data for quickly locating the origin of seized narcotics so that federal and international agencies can take rapid action against dope traffic.

A state highway department uses IR to test durability of traffic paints and to check the specifications of purchased herbicides.

An envelope manufacturer checks the composition of the paper and adhesives it purchases by means of IR.

A commercial laboratory rates the IR spectrophotometer the most useful piece of equipment it owns—"over half our clients have benefited from IR."

A large university has an IR instrument for instruction in undergraduate organic synthesis courses and for graduate research work in organic and physical chemistry.

One hospital reports the use of IR for certain blood and urine analyses; for steroid work; to determine methanol in body fluids; and for other toxicological analyses.

REFERENCES

1. American Petroleum Research Project 44, Chemistry Dept., Carnegie Inst. of Technology, Pittsburgh, Pa.
2. Punch Card Committee of the National Research Council, E. Carroll Creitz, Secretary, National Bureau of Standards, Washington, D. C.

3. COLTHUP, N. B., *J. Opt. Soc. Am.*, **40**, 6 (1950).
4. McMURRAY, H. L., AND THORNTON, V., *Anal. Chem.*, **24**, 318 (1952).

PERKIN-ELMER CORPORATION

CELLULOSE AND FABRICS

Literature search reveals that until the present decade the cellulose research chemist almost completely ignored infrared absorption spectroscopy. The outstanding treatises on the chemistry of cellulose of Heuser, Timmell, Ott, and others either contain no mention of the technique at all or only very scant reference to its use in investigations of the hydrogen bond concept in cellulose. Just as one of the first triumphs of infrared absorption spectroscopy was the study of hydrogen bonding, so its earliest introduction into cellulose research had to do with investigations of this subject. However, it can probably be said that no particularly important contribution of infrared spectra to cellulose chemistry was reported prior to about 1950.

Techniques for Measuring the Infrared Absorption Spectra of Cellulose and Related Materials

Just prior to and into the early 1950's several papers appeared dealing with investigations of cellulosic materials with the aid of infrared absorption. Among these were several papers from a group including Forziati, Rowen, Plyler, and various colleagues from the National Bureau of Standards.¹ This group described a method for preparing a fine cotton powder from which infrared spectra could be obtained as a Nujol mull.^{1b} The method was not entirely satisfactory since grinding results in some changes in structure, as evidenced by loss of crystallinity, and Nujol mulls do not lend themselves to most accurate quantitative measurements of band intensities. In England, Marrinan and Mann² reported several studies on the infrared absorption spectra of cellulosic ma-

terials in the form of films. Films of viscose were prepared by rubbing commercial viscose solution between two glass plates.^{2a} The plates were then slid apart, immersed in 10% ammonium sulphate solution followed by regeneration in 15% sulphuric acid, and then washed with distilled water. Cotton cellulose films were prepared by precipitating the cellulose from cuprammonium or cupriethylenediamine hydroxide solution with acetic acid. The precipitate was separated from solution by centrifuging, washed with distilled water, and films for examination in infrared were prepared by evaporating the aqueous suspension on a microscope cover-slip. Bacterial cellulose was grown from *Acetobacter acetigenum* on Henneburg's medium. Films were washed in caustic soda solution, neutralized with acetic acid, and washed with distilled water. Spectra of such cast films reflect, of course, any changes in structure which accompany the preparation of the film and the technique is not applicable to materials from which such films can not be cast, such as degraded cottons, some chemically modified cottons, etc. O'Connor and co-workers³ at the U. S. Department of Agriculture's Agricultural Research Service, Southern Utilization Research and Development Division, described a method employing the potassium bromide disc technique which they claim: (a) permits measurements of infrared spectra without any modification of the sample during preparation;^{3a} (b) makes possible accurate quantitative infrared absorption measurements^{3a, 3c} and (c) is applicable to all types of natural and synthetic fibers, yarns, and fabrics.^{3b, 3d} A spectrum of native cotton obtained by their technique is shown in Figure 1.

Higgins and his co-workers in Australia have favored solid disc spectra in their investigations of cellulose and cellulosic materials by means of infrared,⁴ but these workers advocate the use of potassium chloride over potassium bromide with the arguments that the chloride has a lower

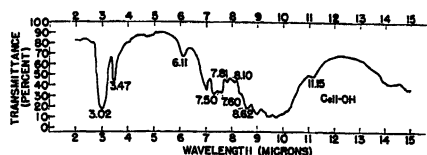


Fig. 1. The infrared absorption spectrum of native cotton obtained by the potassium bromide disk technique.

chemical reactivity, a greater stability to heat, is less hygroscopic, and is easier to grind to a satisfactory particle size. Higgins^{4a} has described in detail a technique using potassium chloride discs and has discussed advantages of the solid disc technique over other methods and the special advantages of the chloride over the bromide. The method recommended calls for the fiber sample to be ground as fine as possible (less than 60 mesh) although Forziati and Rowen,^{1d} and O'Connor *et al.*^{3a, 3b} have shown that grinding to this extent will cause considerable change in the appearance of the infrared absorption spectra arising from decreased crystallinity caused by the grinding. O'Connor *et al.*^{3a} claim that particles ground to not less than 20 mesh are required if the samples are not to be degraded significantly during preparation of the discs. With this consideration of size of sample particles, one definite advantage of potassium bromide over the chloride can be advanced. Cotton is birefringent and the average of its indices of refraction is 1.564. The index for potassium bromide is 1.559. Harvey, Stewart, and Achhammer⁵ have shown, in a recent investigation of index of refraction and particle size as factors in infrared spectrophotometry, that the index of refraction relationship makes it possible to obtain satisfactory spectra of nylon without grinding the samples to a fine powder. In order to avoid losses by scattering, fine particles are required unless indices of refraction between the halide matrix and the sample are very similar. Thus, O'Connor *et al.*^{3a} explain why large pieces of cotton can be introduced into a potassium bromide disc

and still result in a satisfactory spectrum. Potassium chloride has an index of refraction 1.490. Thus, if larger particles are to be used, to avoid decrystallization effects, potassium bromide has a decided advantage over the chloride.

Applications of Infrared to Investigations of Hydrogen Bonding, Crystallinity and Polymorphic Structure of the Cellulose Molecule

Hydrogen Bonding. O'Connor, DuPré, and Mitcham have recently reviewed the subject of hydrogen bonding as investigated by infrared absorption spectra.^{3b} They showed that several chemically modified cottons exhibited spectra which revealed O—H stretching bands at significantly shorter wavelengths than the unmodified controls. Thus, while the spectra of cotton linters exhibited a band attributed to O—H stretching at 3.00 μ , the spectra of methylcellulose and ethylcellulose prepared from them exhibited maxima at 2.94 and 2.92 μ , respectively. A raw cotton exhibited a maximum at 2.98 μ while a cellulose acetate prepared from it reveals a band at 2.85 μ and the spectrum of a carboxymethylated cotton cloth exhibited a maximum at 2.96 μ compared to the 3.00 μ position of the unmodified cotton control. These changes were interpreted as arising from the fact that the chemical reactions were taking place in the amorphous regions and therefore reducing the relative amounts of amorphous O—H groups. The over-all result is a shift in the position of the unresolved O—H band toward the less highly bonded crystalline O—H groups at shorter wavelengths. Rowen and Plyler^{1c} reported this effect in reverse, showing that the regeneration of cellulose from cellulose acetate was accompanied by a shift in the O—H band to slightly longer wavelengths, from 2.86 μ in cellulose acetate to 2.94 μ in regenerated cellulose. These results show that NaCl spectra can be used to indicate some changes in degree of hydro-

gen bonding of the cellulosic materials even though in these spectra the free O—H stretching with maximum about $2.70\ \mu$ is unresolved from O—H bonded stretching vibrations at longer wavelengths.

Brown *et al.*⁶ published results of investigations of the $3.0\ \mu$ region of the spectra of cotton, from samples prepared by casting thin films on finely ground glass plates, with the higher resolution possible with LiF optics. Bands were observed at about 2.98, 3.05, and $3.08\ \mu$ with shoulders on both sides of the $2.98\ \mu$ band. Free O—H stretching gives rise to sharp symmetrical bands, while bonded O—H stretching bands are unsymmetrical with broadening toward the lower frequency (higher wavelength) side. They suggested the measure of "symmetry index"* as a criterion of hydrogen bonding. It should be noted, however, that such measurements could not be made with the resolution afforded with NaCl optics.

Mann and Marrinan^{2b} proposed an ingenious method of investigating the O—H stretching bands of the highly organized crystalline regions of cellulose, without interferences from the broad bands of these stretchings in the amorphous regions, by means of deuteration. Rowen and Plyler^{1a} had previously studied the reaction of heavy water with cellulose and reported that only a small fraction of the O—H groups could be deuterated. Mann and Marrinan, however, confirmed a suggestion of Almin⁷ that the samples of Rowen and Plyler must have partially rehydrogenated before examination. It has been shown that under ordinary conditions deuterium replacement will occur in only the amorphous regions of the cellulose molecules. Thus, after deuteration, the hydroxyl groups of the amorphous region will

appear as O—D stretching bands with maxima at about $3.7\text{--}4.2\ \mu$. The hydroxyls in the crystalline regions will remain as O—H stretchings near $2.8\text{--}3.4\ \mu$. In the amorphous regions there is a range of hydrogen bonds of varying strengths and hence a broad unresolved band. This is the band observed before deuteration. In the crystalline regions, however, there are a discrete number of hydrogen bonds, each giving rise to a definite absorption band. Thus, the spectrum from about 2.8 to $3.4\ \mu$, measured with LiF optics, after deuteration, exhibits four discrete bands. Removal of the unresolved bands arising from hydroxyl groups in the amorphous regions by converting them to O—D bonds makes it possible to observe the bands which are attributable to the O—H stretchings arising from the hydroxyl groups in the crystalline regions only. Mann and Marrinan,^{2a} by means of the spectra of the crystalline region after deuteration, were able to show that in these crystalline regions all the O—H groups were hydrogen bonded in both Cellulose I and Cellulose II. Later this observation was extended to include the hydrogen groups of Cellulose III₁ (Cellulose III prepared from Cellulose I.).^{2c} This deuteration technique of Mann and Marrinan, which has been used to advantage in investigations of crystalline properties of cellulosic materials (see next section), would appear to be a tool capable of yielding still more data for detailed investigations of hydrogen bonding in cellulose.

Other investigations of hydrogen bonding have been described by Ellis and Bath,⁸ who used near infrared absorption from 1.0 to $2.5\ \mu$. They report two bands, one near $1.5\ \mu$, an overtone of the fundamental O—H stretching vibration, and a combination valence-deformation band near $2.0\ \mu$. A sharp but weak band near $1.4\ \mu$ was correlated with the unperturbed (free) hydroxyl stretching overtone and bands with maxima at 1.49 , 1.54 , and $1.58\ \mu$ with bonded O—H stretching. Similarly, bands at approximately

* Symmetry index is defined as the ratio of the band widths on the low and on the high frequency side of the maximum at half band absorbance. The symmetry index for a symmetrical band is thus unity and is greater than unity for bands which are broadened on the low-frequency side.

2.02 and 2.11 μ arise from free and bonded O—H stretching, respectively. In ramie fiber the 2.02 μ band is absent, indicating that all, or practically all, of the hydroxyl groups in natural cellulose fiber are bonded. Mercerization resulted in disappearance of the 1.54 μ band and a progressive shifting of the 2.11 and 2.09 μ bands, indicating that mercerization results in a lesser degree of hydrogen bonding, in agreement with the results reported by O'Connor *et al.*^{3b} and of Rowen *et al.*^{1c} for chemical modification.

Tsuboi⁹ investigated the infrared spectrum of oriented cellulose fibers using polarized radiation. From interpretations of observed polarization effects based on the crystal structure of cellulose, specific assignments were proposed for several bands in the C—H, O—H, C—O and C—C stretching and in the O—H out-of-plane deformation regions. Liang and Marchessault¹⁰ investigated the 3.0 μ region of thin films of valonia cellulose, ramie, and bacterial cellulose crystallites. With polarized infrared radiation they have been able to make specific assignments to parallel and perpendicular, symmetric and anti-symmetric stretching modes of the CH₂ group. With the aid of a model which is compatible with these assignments, and from observed polarization of the bands in the O—H stretching region, a system of hydrogen bonding in Cellulose I was suggested. Two sets of intermolecular hydrogen bonds were proposed: in the 101 plane the C₆ hydroxyls of the antiparallel chains are jointed to the bridge oxygens of the adjacent parallel chains; in the 101 plane the C₆ hydroxyls of the parallel chains are hydrogen-bonded to the bridge oxygens of the adjacent antiparallel chains.

Crystallinity and Polymorphism. Forziati *et al.*^{1b} observed that grinding produced a marked conversion of crystalline to amorphous cellulose. In a later study, Forziati and Rowen^{1d} showed that striking differences were exhibited in the spectra of Cellulose I and Cellulose II in the regions 7–8 μ

and 9–10 μ . However, differences observed in the conversion of Cellulose I to II were almost identical to those observed in the conversion of crystalline Cellulose I to amorphous Cellulose I. O'Connor, DuPré, and Mitcham^{3b} discussed the crystallinity of cellulose. They showed how the spectra of native Cellulose I changed with extent of grinding in a vibratory ball mill and that these changes paralleled those occurring during chemical decrystallization with ethylamine. They pointed out, particularly, that during either mechanical or chemical decrystallization a band at 6.9 μ , arising from a CH₂ deformation, disappears while a weak band at 11.0 μ increases in intensity as the crystallinity decreases. These changes are analogous to the "amorphous" and "crystalline" bands* of nylon¹¹ or of polyethylene terephthalate.¹² O'Connor, DuPré, and Mitcham suggested the use of a ratio of the bands at 6.9 μ and 11.0 μ as a measure of crystallinity index†.^{3b} Values of this index were given for cellulose during successive stages of mechanical decrystallization in a vibratory ball mill and of chemical decrystallization with ethylamine. The indices have been shown to be directly proportional to data obtained by X-ray diffraction measurements,¹³ and have been used in investigations of acetylated and deacetylated cottons¹⁴ and of cotton irradiated with gamma rays from a cobalt 60 source.¹⁵ The use of crystallinity index permits a rapid

* A "crystalline" band is defined as one which decreases in intensity progressively with increase in temperature and finally disappears when the polymer becomes molten. Conversely, an "amorphous" band is one which does not appear in the spectra of the crystalline polymer and becomes more intense with increase in amorphous character.

† "Crystallinity index" is defined as the ratio of the absorbance of the band maximum at about 6.9 μ to the absorbance of the maximum at about 11.0 μ . Absorbancies used to calculate the indices are measured at the two wavelengths by the usual baseline technique.

and simple measurement of relative proportions of crystalline and amorphous regions in a cotton with reasonable sensitivity.

The deuteration technique of Mann and Marrinan^{2b} provides a very precise measure of degree of crystallinity. Results are expressed as a ratio of the absorbance of the maximum of the O—D (amorphous) band at $3.95\ \mu$ to that of the O—H (crystalline) band at $2.98\ \mu$. While this method has the disadvantage of requiring the additional step of deuteration, and has been applied thus far only to cast films, it undoubtedly is the most precise and sensitive method for obtaining crystallinity measurements by means of infrared spectroscopy. This infrared-deuterium technique determines only those hydroxyl groups in which the hydrogen is at liberty to vibrate readily between two positions. Dr. Marrinan concludes that the hydroxyls on the surface of the crystallites as well as those in the amorphous regions will have this freedom of activity, whereas those completely within the crystalline regions will display another type of restraint indicated by the residual infrared curve at the original hydroxyl frequency.

McKenzie and Higgins^{4b} investigated the distribution of two crystalline phases as a function of alkali concentration by means of infrared absorption curves. They presented a series of spectra illustrating changes that occur during the course of mercerization. Changes at 7.0 , 9.0 , 10.1 , and $11.2\ \mu$ were associated with the transition of Cellulose I to Cellulose II. Spectra were presented for cotton and eucalypt cellulose. McKenzie and Higgins quote from T. Yurugi, "when cellulose was treated with NaOH at 20° the amorphous regions increased at the expense of the highly ordered regions." They point out that "in general the influence of the amorphous fraction associated with the Cellulose I crystallites is to make the spectrum more like that of Cellulose II." To this writer the changes in the spectra, as presented by McKenzie and Higgins, could be

accounted for better as changes in crystallinity occurring during the NaOH mercerization treatment rather than as changes in polymorphic form from Cellulose I to Cellulose II. For a given series of samples infrared absorption could be used to follow the course of mercerization. But the infrared spectroscopist would be rather hard put to analyze a mixture of Cellulose I and Cellulose II by means of the absorption bands at 7.0 , 9.0 , 10.1 , or $11.2\ \mu$, since their relative amounts would depend on how much the original Cellulose I in the mixture had been ground or otherwise decrystallized prior to or during mixing with the Cellulose II.

The deuteration technique of Mann and Marrinan,^{2b} however, (because it provides the opportunity for measuring the spectra of the crystalline region over the range of O—H stretching frequencies, 2.7 to $3.4\ \mu$, with complete absence of amorphous portions) affords a real opportunity to differentiate between the various crystalline modifications of cellulose. The spectra, with LiF optics, of the different crystalline modifications of cellulose in the region of O—H stretching after deuteration (and all bands arising from vibrations in the amorphous regions have been removed) showed clear and distinct differences for Cellulose I, Cellulose II, and Cellulose III_I*,^{2d} as seen in Figure 2. Cellulose III_{II} resembled the spectra of Cellulose II and Cellulose IV_I, and IV_{II} those of Cellulose I and II, respectively. Mann and Marrinan concluded, therefore, that only three clearly definable polymorphic forms of cellulose exist, namely I, II, and III_{II}. Each of these can be readily identified and differentiated by means of infrared spectra after deuteration. Studies of this type of spectra with polarized radiation afforded several clues as to the structure of these polymorphs. Hydrogen bonding was

* The subscripts refer to the source of the polymorphic form. Thus III_I is Cellulose III prepared from Cellulose I; Cellulose IV_{II} is Cellulose IV prepared from Cellulose II, etc.

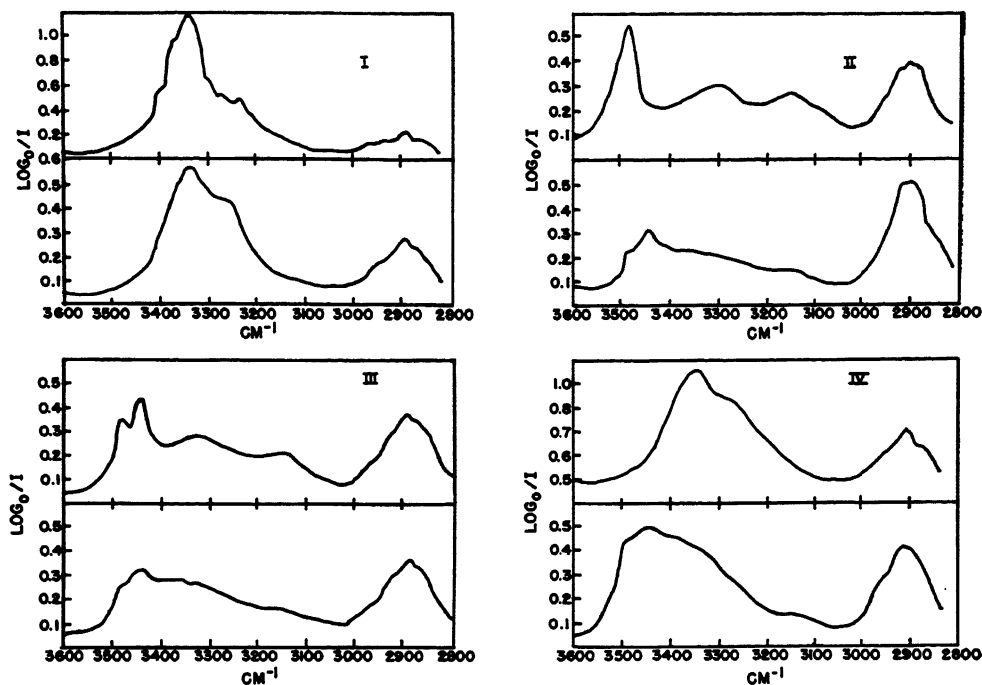
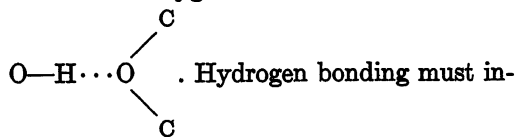


FIG. 2. Infrared absorption spectra in the O-H stretching region, after deuteration, of the different crystalline modifications of cellulose. A. Cellulose I. Types A and B; B. Cellulose II, oriented and un-oriented film; C. Cellulose III, III_I and III_{II} and D. Cellulose IV, IV_I and IV_{II}. (From H. J. Marrinan and J. Mann, *J. Polymer Sci.* Reference 2D with permission of the authors and editor which is gratefully acknowledged.)

shown, from a study with plane-polarized infrared radiation of deuterated samples, to be the type having a system in which bonding is terminated by a hydrogen bond to another oxygen atom O—H...O—H..



volve the ring or a bonded ether oxygen atom in all these crystalline modifications.^{2a}

Oxidation. Infrared absorption has been applied to studies of the oxidation of cellulose with some unexpected results. In their early paper, Rowen, Hunt, and Plyler^{1a} showed that oxidation of cellulose with nitrogen dioxide, which is believed to be highly specific, attacking the primary alcohol group and converting it to a carboxyl, introduced three

bands into the infrared spectra of cellulose, at 5.7, 6.1, and 7.8 μ . Later studies by Rowen and Plyler^{1a} showed that only the 5.7 μ band, arising from a stretching vibration of the C=O in the carboxyl group, should be correlated to oxidation of the cellulose since the other two bands, at 6.1 and 7.8 μ , were found in cellulose nitrate and could be attributed to some nitrogen-oxygen vibration. The earlier study revealed that oxidation of cellulose with periodic acid had little or no effect on its absorption although this agent has been shown chemically to attack the secondary alcohol groups on carbons 2 and 3 and to convert them to aldehyde groups. The anomaly of the non-appearance of the strong C=O stretching of the aldehyde group in such oxidized cottons was increased by subsequent investigations of Forziati, Rowen, and Plyler.^{1a} These investigators described a

method for the quantitative measurement of the carboxyl group in oxidized cotton by means of infrared absorption. They claimed that their "results indicate that the intensity of the absorption of the oxidized celluloses at $5.85\ \mu$ constitutes a fairly satisfactory measure of their carboxyl content even in the presence of appreciable amounts of non-carboxylic carbonyl." In one sample they found and measured as little as 0.19 mmole/g of carboxyl in the presence of 7.37 mmole/g of noncarboxylic carbonyl (by hydroxylamine hydrochloride method.) Thus, as pointed out in a discussion of infrared absorption and oxidation of cellulose by O'Connor, DuPré, and Mitcham,^{1b} "two anomalous results are encountered in the examination of infrared spectra of oxidized cotton cellulose: (a) it can be oxidized under conditions which produce relatively large concentrations of aldehyde (or ketone) groups, but the spectra exhibit no evidence of the well-known, intense C=O stretching vibrations of these groups; and (b) the carboxyl content can be obtained satisfactorily with quantitative accuracy by measurement of the $5.8\ \mu$ C=O stretching vibration of the carboxyl group at wavelengths so close that these bands would be incompletely

resolved from the carbonyl stretchings in NaCl spectra."

A satisfactory explanation for these anomalous results has been provided by Rowen, Forziati, and Reeves.¹¹ They postulate that either or both of the free aldehyde groups of the oxidized cellulose are hydrated by reaction with water. The oxygen atoms are bound either by the formation of aldehyde hydrates, or hemiacetals, or both, as shown in Figure 3.

If a molecule such as illustrated in Figure 3 were produced on periodic acid oxidation of cellulose, no C=O stretching would be expected. Only on further oxidation and the formation of carboxyl groups would the characteristic C=O stretching be observed. The method of Forziati, Rowen, and Plyler¹² for the quantitative determination of carboxyl groups in oxidized cellulose is valid because the carbonyl groups expected are not found. The quantitative results are not obtained, as claimed, in the presence of large quantities of carbonyl—they are accurate only because none of their oxidized cottons contained carbonyl groups *per se*.

Blouin and Arthur¹⁵ used infrared absorption spectra to follow oxidation effects during investigation of gamma radiation on cotton.

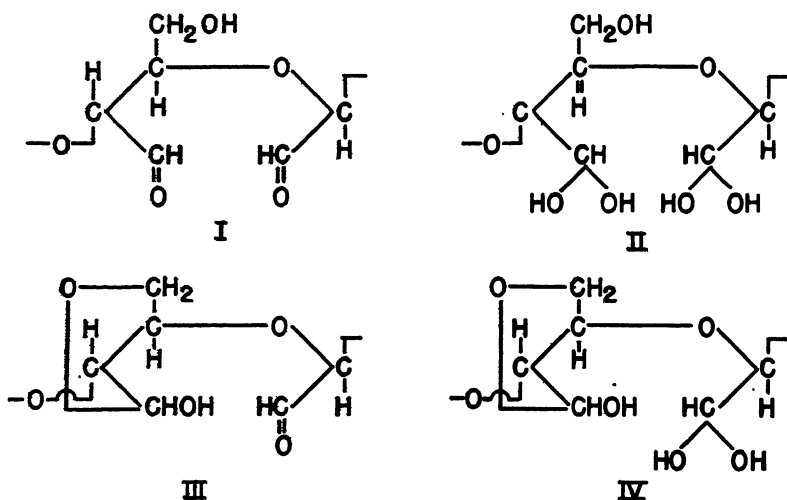


Fig. 3. The molecular structure of periodate-oxidized cellulose.

Measurement of a series of increasing dosages in air, oxygen, and nitrogen revealed no changes in the spectra during the initial stages, although chemical methods showed a continual increase in carbonyl groups. With increasing dosages, however, the infrared absorption curves exhibited weak bands at about $5.8\ \mu$. At about this same stage chemical analyses began to show the presence of carboxyl as well as carbonyl bands. The increase in the intensity of the $5.8\ \mu$ band continued during further radiation and could be shown to be directly proportional to the chemically measured carboxyl content. The band, however, bore no relation whatever to the chemically determined carbonyl content.

Higgins⁴⁰ studied the degradation of cellulose in air by means of infrared spectroscopic examination and obtained results which could be interpreted satisfactorily by the proposal of bound aldehyde groups. He found no, or only insignificant, changes in spectra upon heating at 70°C for periods up to 17 hours at a pressure of 0.5 mm and only slight changes at 175°C at 0.5 mm after 3.5 hours or at $260\text{--}270^\circ\text{C}$ and 0.5 mm. Only on heating for 2 hours in air at $260\text{--}270^\circ\text{C}$ was a strong C=O band obtained. This band dominated the spectrum after heating for 17 hours, and was shown to be mostly carboxyl by its ready conversion to a salt with NaOH, as shown by a shift from $5.8\ \mu$ to the symmetrical and antisymmetrical vibrations of the COO⁻ group at 6.4 and $7.3\ \mu$. Unfortunately, no chemical measurements for carbonyl were reported. It appears likely, however, that the lack of any observed changes in the infrared absorption spectra, until rather long exposures at high temperatures in air, can be explained by the fact that the carbonyl groups formed were completely hydrated and did not change the spectra until the higher temperature heating in air converted them to carboxyl groups.

Higgins and McKenzie⁴¹ described detailed investigations of the periodic acid oxidation of cellulose fibers by means of infrared ab-

sorption spectra using their potassium chloride disc technique. These studies more or less confirm the suggestion of Rowen, Forziati and Reeves¹⁷ that the aldehyde groups of the oxidized glucopyranose residues are hydrated (Figure 3), first by showing that the intensity of the C=O stretching band at $5.8\ \mu$ was dependent not only on the degree of oxidation, but also on the amount of moisture uptake by the sample. The intensity of the band decreases with increased moisture content. Furthermore, the band at about $9.5\ \mu$, which arises from either an O—H deformation or a C—O stretching of the primary C—O—H group, or a coupling of both of these vibrations (and which, in any case, represents a vibration correlated to a primary O—H group) decreases and is eliminated on severe oxidation. If the periodic acid oxidation occurs at the secondary alcohols, disappearance of this primary alcohol can be accounted for by the hemiacetal formation suggested by Rowen, Forziati, and Reeves.

Higgins and McKenzie discussed changes in several of the cellulose bands during periodic acid oxidation. The band at $8.6\ \mu$, assigned by Forziati and Rowen¹⁴ to a vibration of the glucopyranose ring, and by O'Connor, DuPré, and McCall³⁸ to a C—O stretching or O—H deformation associated with a hydroxyl group attached to the ring, progressively decreases in intensity and definition. This change in intensity on oxidation could result either from ring cleavage or from the conversion of the secondary hydroxyls to ketonic groups. A band at about $11.2\ \mu$ is displaced to long wavelengths, about $11.35\ \mu$, on oxidation. Barker *et al.*¹⁶ suggest that this band arises from a C—H deformation mode in which the hydrogen atom on the C₁ position is involved. Higgins and McKenzie attribute the observed frequency shift to bending force constant changes arising from ring scission. Decrease in a band at about $9.0\ \mu$, associated with deformation of secondary O—H groups, is in agreement with the accepted specific attack of the periodic

acid on the secondary O—H groups. Similarly, the absorption band at $7.3\ \mu$, which has been assigned to an O—H deformation mode, loses definition and is reduced in intensity. A band at $7.95\ \mu$, attributed to a C—O stretching of the carboxyl group, arises in the oxidized samples. This band can be reduced by treatment of the oxidized cellulose with sodium hydroxide, confirming its assignment, since this treatment would result in elimination of the carboxylic C=O on salt formation, represented by the vibrations of the new COO⁻ group. However, as considerable absorption persists after this treatment, Higgins and McKenzie concluded that some aldehyde or ketone absorption is present. A sharp band at about $7.0\ \mu$ becomes poorly defined in oxidized samples. This band is assigned to a CH₂ deformation and may represent oxidation at the C₆ position, or may be accounted for as destruction of crystallinity. This is the band that O'Connor *et al.*^{3b} used for their infrared crystallinity index. The whole region from 7.0 to $11.0\ \mu$ becomes diffuse and characteristic of an amorphous polymer as the oxidation process continues. There is, therefore, little doubt that the crystallites are attacked as well as the amorphous regions.

Applications to Modified Cotton and Synthetic Fibers and Fabrics

Modified Cotton. With the exception of the experiments with oxidized cellulose, all applications of infrared absorption which have been described have dealt with vibrations of the active hydroxyl group or with C—H modes which have been linked to crystalline or amorphous character. They have been concerned with only the cellulose molecule. Today one of the principal research activities of the cellulose chemist is the chemical modification of the cellulose molecule. He has been investigating the replacement of hydroxyls with a variety of organic functional groups, either directly or through the formation of intermediate compounds,

to impart to a fiber or a fabric special properties for specific end uses. This chemical modification of cotton has created an additional task, or a new opportunity, for the chemical application of infrared absorption spectroscopy. Infrared spectra can be used as a simple, rapid, and accurate tool to identify the manner in which a cotton has been modified and to measure the extent to which it has been modified. Spectra can be used to ascertain whether a planned modification has proceeded as expected to yield the desired chemical modification and to determine the efficiency of the modification reaction by measuring relative proportions of the undesirable and unwanted side products. O'Connor, DuPré, and McCall^{8c} and O'Connor^{3d} have described application of their KBr disc technique to the analysis of several chemically modified cottons.

In Figure 4 are shown the infrared spectra of some cottons modified by direct replacement of the hydroxyl groups. Figure 4 (A) is the spectra of partially acetylated cotton, probably the oldest and best known modification of cotton. Comparison of this spectrum with that of an unmodified cotton, Figure 4 (C), shows that the acetylation can be readily recognized, in the spectrum of the modified cotton, by the appearance of the strong band at $5.7\ \mu$ arising from a stretching vibration of the C=O group of the ester. This band can be used to measure quantitatively the degree of acetylation, as shown in Figure 5 (a). The acetate group can also be identified by the appearance of the characteristic band, arising from a C—O stretching at $8.10\ \mu$. The spectrum of an example of an etherification, the cyanoethylation of cotton by treatment with acrylonitrile in the presence of sodium hydroxide and water, is shown in Figure 4 (B). Again comparison of this spectrum with that of the unmodified cotton reveals the presence of the additional characteristic band at $4.45\ \mu$ arising from a stretching vibration of the C≡N nitrile group. Quantitative measurement of this

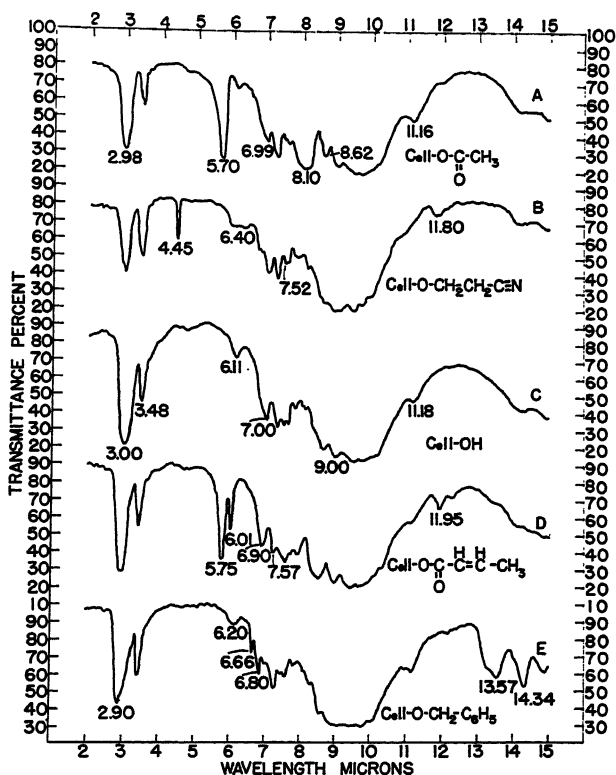


FIG. 4. Infrared absorption spectra of cottons modified by direct replacement reactions. A. Partially acetylated (PA) cotton; B. Partially cyanoethylated (CN) cotton; C. Native, unmodified cotton; D. Cotton esterified with crotonic acid; and E. Cotton etherified with benzyl chloride. All as potassium bromide disk spectra.

group is illustrated by the Beer-Lambert curve in Figure 5(b). The infrared spectrum of a cotton esterified with the unsaturated aliphatic acid, crotonic acid, is seen in Figure 4 (D). This spectrum, when compared to that of the unmodified cotton, reveals in addition to the strong C=O stretching band at 5.75 μ , a sharp band with maximum at 6.01 μ . This latter band arises from a vibration associated with C=C stretching and can be used to differentiate cellulose modified by esterification with unsaturated aliphatic acids. The spectrum of a cellulose etherified with benzyl chloride to produce partially benzylated cotton, Figure 4 (E), again by comparison with the spectrum of untreated cotton, affords identification of the modification. Etherification is, of course, readily dis-

tinguished from esterification by means of infrared spectra by the absence of the intense characteristic C=O stretching band at about 5.7 μ . Benzylated cellulose can be differentiated from etherification with aliphatic unsaturated acids by the absence of the sharp C=C stretching at 6.01 μ and by the appearance of two bands arising from C=C stretching modes within the aromatic ring at 6.2 and 6.7 μ . The latter of these two bands is the stronger, indicating that there is no conjugation with the benzene ring. The identification can also be made and the extent of benzylation quantitatively measured by means of bands at 13.57 and 14.34 μ arising from C—H deformations about the aromatic ring.

Chemical modification of cotton has not

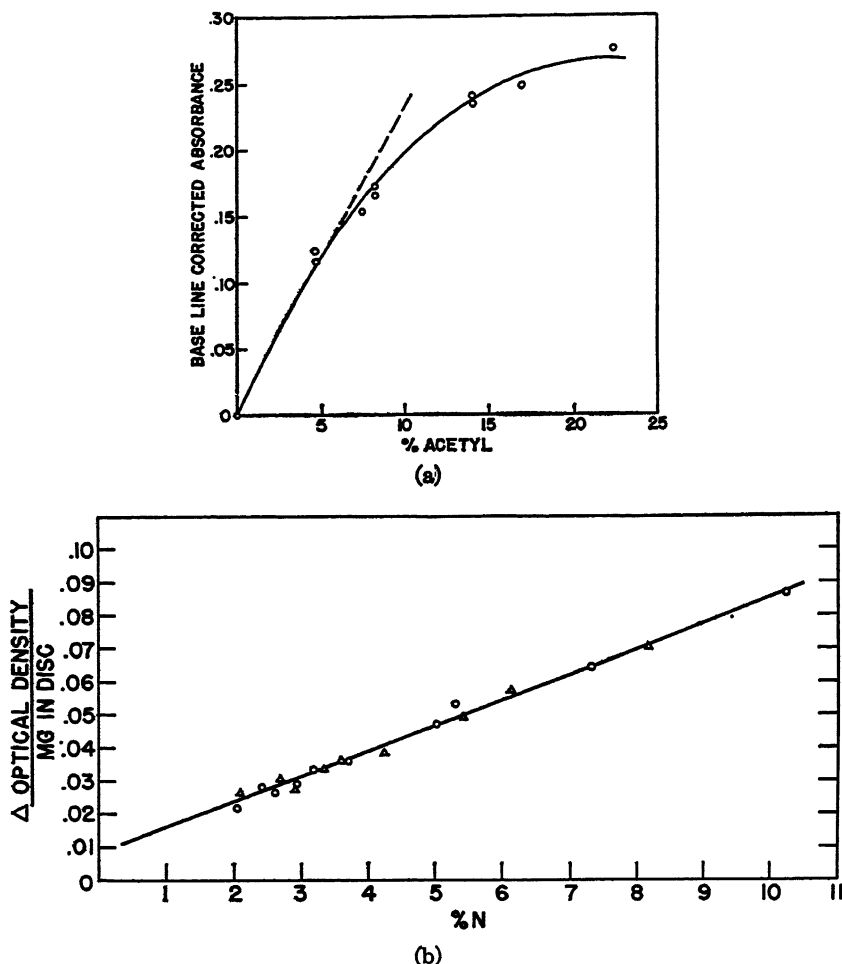


FIG. 5. Beer-Lambert relations for partially acetylated and partially cyanoethylated cottons.

yet been restricted to the use of reagents which will react readily with the hydroxyl group. One technique for introducing into the cellulose molecule a group which will not react, or will not react readily with the hydroxyl group, is to introduce a chemically active group which is then replaced by the desired group. Replacement of the sulfonyl groups in mesylated cotton, that is, cotton treated with methyl sulfonyl chloride or in tosylated cotton, treatment with *p*-toluene sulfonyl chloride, has been one of the more successful types of replacement reaction. Both mesyl- and tosyl-cellulose have been known to the cellulose chemist for a long time. In

Figure 6 the spectra of cottons modified by this type of replacement reaction are shown. Figure 6 (A) is the spectrum of mesylated cotton.

A mesylated cotton can be readily identified by its infrared spectrum by appearance of an unusual C—H stretching band at 3.30μ arising from a C—H stretching of the methyl group adjacent to the SO_3 ; by two bands at about 7.3 and 8.5μ , arising from the covalent sulfonate group $\text{—O—SO}_3\text{—R}$; and by bands at 12.08 and 13.25μ arising from C—O—S and C—S vibrations, respectively. The mesylated cotton was subsequently treated with the sodium salt of *p*-methyl-

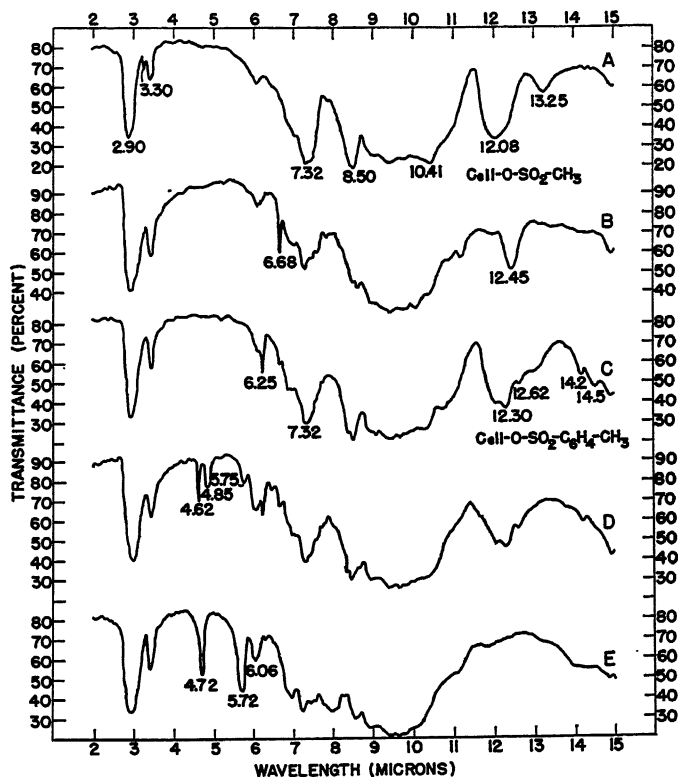


FIG. 6. Infrared absorption spectra of cottons modified by replacement reactions. A. Mesylated cotton; B. Mesylated cotton treated with sodium salt of *p*-methylthiophenol; C. Tosylated cotton; D. Tosylated cotton treated with potassium thiocyanate; and E. A cotton first acetylated, then mesylated, and then treated with sodium azide. All as potassium bromide disc spectra.

thiophenol. The spectrum of the product, Figure 6 (B), is characterized by the strong band with maximum at 6.68μ . This band is seen in the spectrum of the *p*-methylthiophenol reagent. Its presence can be used to verify the reaction and its intensity to measure the extent of the replacement. The complete absence of the bands which identify the mesyl group confirm, in this example, that the replacement reaction has been quantitative.

A tosylated cellulose has been further treated with potassium thiocyanate to produce the replacement product the spectrum of which is shown in Figure 6 (D). Tosylated cotton (Figure 6, C) can be identified by bands at 7.3 and 8.5μ arising from the covalent sulfonate group $\text{—O—SO}_2\text{—R}$, very

similar to those observed in the spectrum of mesylated cellulose. Tosylation can be differentiated from mesylation, however, by the absence of the 3.30μ band and by the appearance of either the $\text{C}=\text{C}$ stretching bands of the aromatic ring at 6.25 and 6.7μ or by the 14.2μ aromatic ring band (C—H deformations about the aromatic ring). Two bands in the final replacement product (Figure 6, D) at 4.62 and 4.85μ , assigned to the $\text{C}\equiv\text{N}$ group, identify the type of replacement and could be used to measure the extent of the replacement reaction.

In Figure 6 (E) infrared absorption has been used to identify a multimodified cellulose. This is the spectrum of a cotton modified by three successive reactions. The sample was first acetylated, then mesylated, and the

mesyl groups replaced by treatment with sodium azide in *N,N*-dimethyl formamide. The acetyl group is identified by the usual carbonyl band at $5.72\ \mu$. Complete replacement of the mesyl group is shown by the absence of any trace of the 3.3 and $12.1\ \mu$ bands. The azide can be identified and might be quantitatively measured by the band at $4.72\ \mu$ arising from a $\text{N}\equiv\text{N}$ vibration.

Some chemically modified cottons have been found to be much more readily susceptible to certain modifications than the original unmodified cotton. Thus aminized cotton (AM cotton) and carboxymethylated cotton (CM cotton) can be modified more readily or to a greater extent than unmodified cottons. Figures 7 (A) and 7 (B) are the spectra of aminized cotton before and after further mod-

ification by reaction with nitromethane. AM cotton can be readily recognized by its infrared spectrum by either the broadening of the $\text{O}-\text{H}$ stretching vibrations about $3.0\ \mu$ due to unresolved $\text{N}-\text{H}$ stretching, or by the appearance of the characteristic $\text{N}-\text{H}$ deformation at $6.40\ \mu$. After treatment with nitromethane the replacement product can be identified by the strong $\text{N}=\text{O}$ stretching band at $6.47\ \mu$ (Figure 7, B). Carboxymethylated cotton is prepared by reaction of cellulose with a solution of monochloroacetic acid, followed by treatment with a strong solution of sodium hydroxide. The reaction product will be in the form of a sodium salt and the infrared absorption spectra will not reveal the expected $\text{C}=\text{O}$ stretching between 5.7 and $5.8\ \mu$ (Figure 7, C). However CM cotton can be

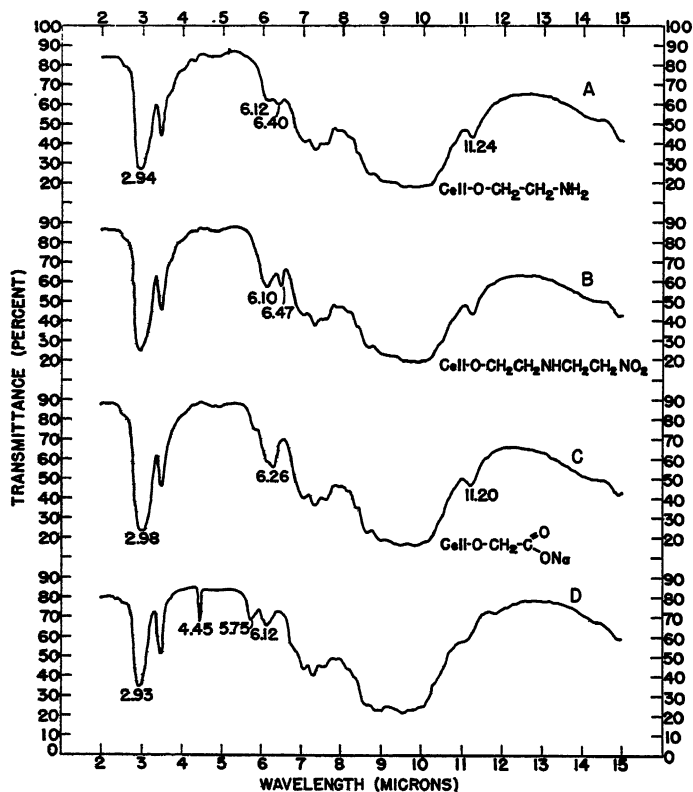


FIG. 7. Infrared absorption spectra of multi-modified cotton. A. Aminized (AM) cotton; B. AM cotton treated with nitromethane; C. Carboxymethylated (CM) cotton; and D (CM) cotton treated with acrylonitrile. All potassium bromide disk spectra.

recognized by the appearance in its spectra of the characteristic carboxylate ion band COO^- at $6.1\text{--}6.2\ \mu$. Identification of this band can be established by an acid wash which converts the COO^- to the free acid with the C=O stretching band at $5.8\ \mu$. Figure 7 (D) is the spectrum of a CM cotton further modified by cyanoethylation with acrylonitrile. The extent of the cyanoethylation reaction is indicated by the $\text{C}\equiv\text{N}$ nitrile group intensity at $4.45\ \mu$. The degree of carboxymethylation can be measured quantitatively, even after the cyanoethylation reaction by measurement of the intensity of the $5.75\ \mu$ C=O stretching band.

Thus, in multiple modified cottons the two modifications can be identified and quantitatively estimated in the presence of each other by means of infrared absorption spectra. In replacement reactions this tool can be used to identify the replacement group, to measure it quantitatively and to confirm the complete absence of the intermediate in the final product.

Resin-Treated Fabrics. Extending the techniques used successfully for the investigation of chemically modified cottons, by means of infrared absorption spectra, to resin-treated cottons has not been entirely satisfactory. The main problem involved in the examination of these types of samples is sensitivity. Usually the amount of resin in a treatment, to impart wash-wear or other specific properties to a cotton, is quite low and often, too, the types of organic reagents used do not have a characteristic functional group which gives rise to any particularly intense band. A technique to increase the sensitivity of the infrared method is required. The most obvious approach is probably a combination of differential infrared absorption measurements with a linear scale expander. The differential technique, that is measuring the spectra of the treated cotton against a disc containing the untreated cotton, will permit the recognition of specific groups free from the spectrum of cellulose.

Linear scale expansion should permit these weak bands to be examined and quantitatively measured at the low concentration levels that are often found in these resin treated fabrics. Experiments on this approach are in progress, but considerably more experimental work is needed in this area.

Forziati and co-workers¹⁷ have described a method for the identification of textile coatings by means of infrared spectroscopy which involves extraction of the sample with a series of suitable solvents and identification of the textile coating in the spectra of the series of extracts.

Other Natural and Synthetic Fibers. O'Connor, DuPré, and Mitcham¹⁸ showed that their KBr disc technique would give good spectra of several natural and synthetic fibers. Hurtubise¹⁹ extended the method to other types of fabrics. A task group has been established under Committee D-13 of the American Society for Testing Materials to study methods for measuring the infrared absorption spectra of natural and synthetic fabrics. In the preparation of discs two problems may be encountered which if not overcome will result in unsatisfactory spectra. First, the sample must be intimately mixed with the KBr. Some materials, including certain types of synthetic fibers, when finely ground become somewhat plastic and sticky, forming masses of the material rather than mixing with the KBr matrix. Several techniques have been described to overcome this tendency, including mixing in a vibratory ball mill where there is a shearing as well as mixing action, and mixing a larger concentration of sample than is required and diluting the mixture with additional KBr. A method found particularly satisfactory is the addition of a volatile solvent, forming a slurry of the sample and KBr. This slurry is thoroughly mixed and the volatile solvent pumped off. With sufficient care satisfactory spectra can be obtained by one technique or

INFRARED SPECTROPHOTOMETRY

TABLE I. Fifty Infrared Absorption Bands of Particular Significance in the Investigation of Modified Cottons

Unmodified cotton spectra—approx. position of band maxima— μ	Vibrating group most probably giving rise to observed absorption band	Modified cotton spectra—approx. position of band maxima— μ	Specific use in application of infrared absorption spectra to cotton and modified cotton
2.8–3.2	Free O—H and bonded O—H . . . stretching		Investigations of extent and type of hydrogen bonding [11]
	N—H stretching	3.0	Appears as a broadening of the 2.8–3.2 μ O—H stretching band in the spectra of amino-cellulose
	C—H stretching of CH ₃ group adjacent to SO ₃ group	3.30	Identification of mesylation, especially to differentiate from tosylation
	C—H stretching of C—H and CH ₃ groups		Characteristic of all cottons
	C—H stretching of CH ₃ group	3.45–3.55	Indicates methyl or ethyl cellulose
	C $\equiv$ N stretching	4.45	Identification and quantitative measurement of cyanoethylation
	C $\equiv$ N stretching	4.62 and 4.85	Characteristic of cotton modified by replacement reaction with thiocyanate
	N $\equiv$ N stretching	4.72	Identification and quantitative measurement of cotton modified by replacement reaction with azide
	C=O stretching (anhydride)	5.57	Coupled with deformation bands in 13 μ region, verifies that esterification with anhydride has been accomplished without breaking anhydride ring, e.g., aconitic anhydride
	C=O stretching	5.58	In absence of evidence of anhydride ring, may indicate position of substituent
	C=O stretching (ester)	5.75	Identification and quantitative measurement of esterification
	C=O stretching (acid)	5.85	If this band appears only after a HCl wash it can be used to differentiate esterification and etherification with an acid. Absence of this band after esterification with a dicarboxylic acid may indicate cross-linkage
	C=O stretching	5.98	May indicate esterification with a polybasic acid
	C=O stretching (amide)	6.00–6.06	Indicates modification to form an amide, e.g., carbamoylethylation with acrylamide; replacement of mesyl with N,N-dimethylformamide; replacement of cyanoethyl with hydroxylamine (see 6.30 μ)
	C=C stretching (aliphatic)	6.10	Indicates modification with aliphatic unsaturated compound or aromatic compound containing unsaturated side chain
6.13	Absorbed H ₂ O		Characteristic of all cottons
	C=C stretching (aromatic ring)	6.25	Evidence for acylation with aromatic compound. Means for differentiation between tosylation and mesylation (see 6.70 μ)

TABLE I. (Continued)

Unmodified cotton spectra—approx. position of band maxima— μ	Vibrating group most probably giving rise to observed absorption band	Modified cotton spectra—approx. position of band maxima— μ	Specific use in application of infrared absorption spectra to cotton and modified cotton
	N—H deformation (amide)	6.30	See 6.00–6.06 μ
	COO ⁻ ion stretching mode	6.2–6.4	Evidence for etherification with an acid and resulting salt formation
	N—H deformation	6.30	Probably indicates amino-cellulose or 2-amino-ethyl cellulose (see 3.0 μ)
	C=C stretching of conjugated aromatic ring	6.32	Evidence for acylation with benzoic type reagent
	C=C stretching (aromatic ring)	6.7	See 6.25 μ
6.96	CH ₂ wagging		Measure of degree of crystallinity [11]
7.26	C—H deformation		Splitting of this band into two components indicates esterification with isobutyl
	S=O stretching of sulfonate, —O—SO ₂ —R group	7.3	Evidence for mesylation or tosylation (see 8.5 μ)
7.46	O—H in-plane deformation		Characteristic of all cottons
7.58	O—H deformation and/or CH ₂ wagging		Characteristic of all cottons
7.78	O—H deformation and/or CH ₂ wagging		Characteristic of all cottons
	P=O stretching	8.0	Evidence for modification with phosphoryl—not observed in spectra of any modified cottons examined—see text
8.02	O—H deformation and/or CH ₂ wagging		Characteristic of all cottons
	S=O stretching of sulfonate, —O—SO ₂ —R group	8.5	See 7.3 μ
8.61	Unassigned		Characteristic of all cottons
8.95	Unassigned		Characteristic of all cottons
	P—O—C stretching	9.5–9.7	Evidence for modification with phosphoryl (see 8.0 μ)
9.45	Unassigned		Characteristic of all cottons
9.71	Unassigned		Characteristic of all cottons
	C—H deformation	10.62	Evidence for methyl cellulose
11.20	CH ₂ wagging		Measure of degree of crystallinity [11]
	C—H deformation	10.85 and 11.30	Evidence for ethyl cellulose
	C—H deformation	11.82	Evidence for esterification with isobutyric acid
	C—O—S stretching	12.1–12.3	Identification and quantitative measurement of mesylation or tosylation
	C—S (tosyl) stretching	12.62	Identification of tosylation
	C—H deformation	12.88	Evidence for esterification with capric acid
	PhCH ₂ C=O	13.0–13.1	Identification and quantitative measurement of esterification with phenylacetic acid type reagent
	C—S (mesyl) stretching	13.25	Identification of mesylation
	C—H bending about anhydride ring	13.0 and 13.6	Verifies esterification with anhydride (see 5.57 μ)
	C—H bending about aromatic ring	14.1–14.4	Identification and quantitative measurement of modification with aromatic compound

another, the preparation of good discs becoming more of an art than a science.

A second factor which adversely affects the quality of KBr disc spectra is the relationship between the index of refraction of the sample and of the KBr. Harvey *et al.*⁵ have shown that the closer the match in index of refraction the less the requirement for fine grinding of the sample and matrix. O'Connor, DuPré, and McCall^{3a} reported that they could obtain satisfactory spectra of cotton in KBr discs even though the cotton was not ground at all, but merely cut in a Wiley mill. Although a 20-mesh screen was adopted for analytical control, satisfactory discs were made with relatively large pieces of cotton. This was explained, on the basis of the report of Harvey *et al.*, by the fact that the average index of refraction of cotton was very close to that of KBr. If, however, the index of refraction of a material is considerably different from that of the KBr, a satisfactory disc may not be obtained regardless of the degree of grinding. In these cases recourse must be had to the use of another matrix, with an index of refraction closer to the sample. Harvey *et al.*⁵ comment on the use of other matrices and demonstrate the improvement in spectral quality in some illustrations. However, this is another phase of solid state infrared spectra which needs considerably more experimental investigation.

The advantages of infrared absorption spectroscopy in cellulose chemistry, and its applications to fibers and fabrics, both natural and synthetic, have been recognized and described in recent review articles by Hurlbise,¹³ Mann,²⁰ and Higgins.⁴⁰ A list of fifty infrared absorption bands of particular significance in the investigation of modified cottons, taken from the publication of O'Connor, DuPré, and McCall^{3a}, is reproduced in Table 1.

REFERENCES

- 1a. ROWEN, JOHN W., HUNT, C. M., AND PLYLER, E. K., "Absorption Spectra in the Detection

of Chemical Changes in Cellulose and Cellulose Derivatives," *J. Research, Natl. Bur. Standards*, **39**, 133-40 (1947); *Textile Research J.*, **17**, 504-11 (1947); 1b "Cotton Powder for Infrared Transmission Measurements," F. H. FORZIATI, W. K. STONE, J. W. ROWEN, AND W. D. APPEL, *J. Research, Natl. Bur. Standards*, **45**, 109-13 (1950); 1c. "Effect of Deuteration, Oxidation, and Hydrogen-Bonding on the Infrared Spectrum of Cellulose," J. W. ROWEN AND E. K. PLYLER, *J. Research, Natl. Bur. Standards*, **44**, 313-20 (1950); 1d. "Effect of Changes in Crystalline Structure on the Infrared Absorption Spectrum of Cellulose," F. H. FORZIATI, AND J. W. ROWEN, *J. Research, Natl. Bur. Standards*, **46**, 38-42 (1951); 1e. "Spectrophotometric Determination of Carboxyl in Cellulose," F. H. FORZIATI, J. W. ROWEN, AND E. K. PLYLER, *J. Research, Natl. Bur. Standards*, **46**, 288-91 (1951); 1f. "Spectrophotometric Evidence for the Absence of Free Aldehyde Groups in Periodate Oxidized Cellulose," J. W. ROWEN, F. H. FORZIATI, AND R. E. REEVES, *J. Am. Chem. Soc.*, **73**, 4484-7 (1951).

- 2a. MARRINAN, H. J., AND MANN, J., "A Study by Infrared Spectroscopy of Hydrogen Bonding in Cellulose," *J. Appl. Chem. (London)*, **4**, 204-11 (1954); 2b. "The Reaction Between Cellulose and Heavy Water, Part I. A Qualitative Study by Infrared Spectroscopy, Part II. Measurement of Absolute Accessibility and Crystallinity, Part III. A Quantitative Study by Infrared Spectroscopy," J. MANN, AND H. J. MARRINAN, *Trans. Faraday Soc.*, **52**, 481-7, 487-92, 492-7 (1956); 2c. "Crystalline Modifications of Cellulose, Part II. A Study with Plane-Polarized Infrared Radiation," J. MANN, AND H. J. MARRINAN, *J. Polymer Sci.*, **32**, 357-70 (1958); 2d. "Infrared Spectra of Crystalline Modifications of Cellulose," H. J. MARRINAN AND J. MANN, *J. Polymer Sci.*, **21**, 301-11 (1956); 2e. "Infrared Spectroscopy and Fibers," J. MANN, *Skinner's Silk and Rayon Record*, **28**, 1262-5 (1956).
- 3a. O'CONNOR, ROBERT T., DUPRÉ, ELSIE F., AND MCCALL, E. R., "Infrared Spectrophotometric Procedure for Analysis of Cellulose and Modified Cellulose," *Anal. Chem.*, **29**, 998-1005 (1957); 3b. "Applications of Infrared Absorption Spectroscopy to Investigations of Cotton and Modified Cottons, Part I. Physical and Crystalline Modifications and Oxidation," ROBERT T. O'CON-

- NOR, ELSIE F. DUPRÉ, AND DONALD MITCHAM, *Textile Res. J.*, **28**, 382-92, (1958); 3c. "Applications of Infrared Absorption Spectroscopy to Investigations of Cotton and Modified Cottons; Part II, Chemical Modifications," ROBERT T. O'CONNOR, ELSIE F. DUPRÉ, AND E. R. MCCALL, *Textile Res. J.*, **28**, 542-54 (1958); 3d. "Infrared Spectra of Cellulose Modifications," ROBERT T. O'CONNOR, Presented at 135th Annual Meeting, Am. Chem. Soc., Boston, Mass., April 5-10, 1959.
- 4a. HIGGINS, H. G., "The Use of Potassium Chloride Disks in the Infrared Examination of Fibrous Cellulose and Other Solid Materials," *Australian J. Chemistry*, **10**, 496-501 (1957); 4b. "The Structure and Properties of Paper, II. The Influence of Alkali on the Infrared Spectra, Bonding Capacity and Beating Response of Wood and Cotton Fibres," A. W. MCKENZIE, AND H. G. HIGGINS, *Svensk Papperstidn.*, 1958, 893-901; 4c. "The Degradation of Cellulose in Air at 250° C as Shown by Infrared Spectroscopic Examination," H. G. HIGGINS, *J. Polymer Sci.*, **28**, 645-8 (1958); 4d. "The Structure and Properties of Paper. X. Periodic Acid Oxidation on Cellulose Fibres and Its Influence on Paper Properties," H. G. HIGGINS, AND A. W. MCKENZIE, *Australian J. Appl. Sci.*, **9**, 167-82 (1958); 4e. "The Structure and Properties of Paper IX. Some Critical Problems," H. G. HIGGINS, *AP-PITA*, **12**, 1-24 (1948).
 5. HARVEY, M. R., STEWART, J. E., AND ACHHAMMER, B. G., "Index of Refraction and Particle Size as Factors in the Infrared Spectrophotometry of Polyvinyl Chloride," *J. Research Natl. Bur. Standards*, **56**, 225-35 (1956).
 6. BROWN, L., HOLLIDAY, P. AND TROTTER, I. F., "The Absorption Spectra of Some Cellulose Derivatives in the 3μ Region," *J. Chem. Soc.*, **1951**, 1532-9.
 7. ALMIN, K. E., "The Reaction Between Cellulose and Heavy Water," *Svensk. Papperstidn.*, **55**, 767-70 (1952).
 8. ELLIS, J. W., AND BATE, JEAN, "Hydrogen Bridging in Cellulose as Shown by Infrared Absorption Spectra," *J. Am. Chem. Soc.*, **62**, 2859-61 (1940).
 9. TSUBOI, MASAMICHI, "Infrared Spectrum and Crystal Structure of Cellulose," *J. Polymer Sci.*, **25**, 159-171 (1957).
 10. LIANG, C. Y., AND MARCHESSAULT, R. H., "Infrared Spectra of Crystalline Polysaccharides. I. Hydrogen Bonds in Native Celluloses," *J. Polymer Sci.*, **37**, 385-95 (1959).
 11. SANDELMANN, I., AND KELLER, A., "Crystallinity Studies of Polyamide by Infrared, Specific Volume, and X-ray Methods," *J. Polymer Sci.*, **19**, 401-35 (1956).
 12. DANIELS, W. W., AND KITSON, R. E., "Infrared Spectroscopy of Polyethylene Terephthalate," *J. Polymer Sci.*, **33**, 161-70 (1958).
 13. SEGAL, L., CREEELY, J. J., MARTIN, JR., A. E., AND CONRAD, C. M., "An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer," *Textile Research J.* (In Press).
 14. BAILEY, A. V., HONOLD, EDITH, AND SKAU, E. K., "Topochemical Mechanism Involved in the Preparation and Deacetylation of Partially Acetylated Cottons," *Textile Research J.*, **28**, 861-73 (1958).
 15. BLOUIN, F. A., AND ARTHUR, J. C., JR., "The Effect of Gamma Radiation on Cotton. I. Some of the Properties of Purified Cotton Irradiated in Oxygen and Nitrogen Atmospheres," *Textile Research J.*, **28**, 198-204 (1958).
 16. BARKER, S. A., BOURNE, E. J., STACEY, M., AND WHIFFEN, D. H., "Infrared Spectra of Carbohydrates. I. Some Derivatives of D-Glucopyranose," *J. Chem. Soc.*, **1954**, 171-6.
 17. FORZIATI, F. H., HITE, R. T., AND WHEARTON, M. K., "Identification of Textile Coatings by Infrared Spectroscopy," *Am. Dyestuff Reporter*, **9**, No. 4, 29-33 (1960).
 18. HURTUBISE, FERNAND, "Applications of Infrared Spectroscopy to Cellulose Chemistry," *Can. Textile J.*, **76**, 53-60 (June 12, 1959).

ROBERT T. O'CONNOR

CELLULOSE AND ITS DERIVATIVES: NEAR INFRARED SPECTROSCOPY

Near infrared spectroscopy may be applied to the study of cellulose and cellulose derivatives as a strictly analytical tool or as a means of obtaining physical information concerning molecular structure and behavior. The high sensitivity of the lead sulfide cell and the intense emission of the ordinary tungsten lamp permit rapid and accurate measurement in the near infrared region provided the dispersing monochromator is capable of good resolving power.¹

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The analytical possibilities of this region are numerous and include such fields as the determination of (1) plasticizers, (2) water, (3) acetyl content (or residual hydroxyl), (4) modifiers, and (5) length of side chains. Of course, there is the limitation that the components of the sample which are being analyzed (analytes) must possess differences in molecular structure in some way connected with the bound hydrogen atoms. Near infrared spectra are not characterized by skeletal vibration bands but by overtone and combination bands of hydrogenic stretching vibrations. If the unknown component of the sample in question contains an OH, SH, NH, or CH linkage which is different from the major constituent of the sample, the analysis may be readily accomplished.²

The major contribution of near infrared spectroscopy to the physical chemistry of cellulose is connected with the study of hydrogen bonding. Cellulose contains three hydroxyl groups per glucose unit and these are replaced in part or in whole in cellulose derivatives. The hydrogen bonds which can form between these hydroxyl groups and any Lewis base group such as oxygen or nitrogen in solvents or plasticizers play dominant roles even though 95% of the hydroxyl groups may be substituted. In the following

discussion, use will be made of the near infrared spectra of simple alcohols to illustrate the type of information that can be obtained. This will be followed by a few applications to cellulose acetate solutions.

In the free or unassociated state a hydroxyl group will absorb energy at approximately 2.75 and 1.40 μ . The 2.75 μ band is due to the fundamental OH stretching vibration while the 1.4 μ band is the first overtone of this band. These bands are very sharp and intense. When the hydrogen of the hydroxyl group can form a bridge to a Lewis base, the 2.75 μ band is displaced to longer wavelengths and is broadened. The extent of the shift of the band is related to the strength of the hydrogen bond.³

If the intensity of the band is integrated with wavelength, the associated OH fundamental band is found to be greater than that of the corresponding unassociated band. However, in the case of the overtone band, the intensity (either peak or integrated) of the band of the associated molecule is considerably less than that of the unassociated molecule. As a general rule, it will be found best to use the fundamental region for studying hydrogen bonded OH groups and the overtone region for studying "free" hydroxyl groups.

As an example of this, Figure 1 shows the spectra of ethanol in the fundamental and overtone regions and at three concentrations. Compensation has been made for the weak absorption of the impurities in the solvent, carbon tetrachloride. By changing the cell length inversely with the solute concentration, the same amount of ethanol is maintained in the optical path at each of the three concentrations. The spectrum of the pure ethanol shows no sign of any sharp unassociated OH band indicating complete association of the ethanol molecules. The hydrogen bonded OH band is observed to be quite broad with a maxima around 3 μ and 1.6 μ . The exact location of the associated band in the overtone region is not readily ascer-

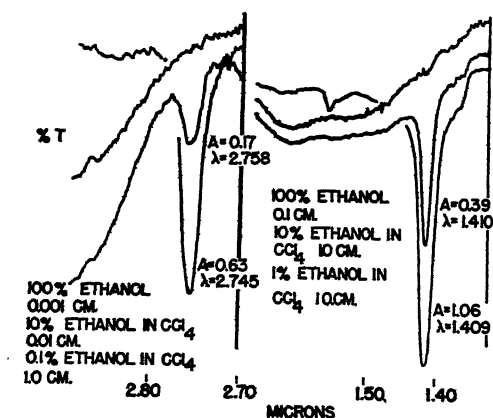


FIG. 1. Fundamental and first overtone spectra of OH stretching vibration of solutions of ethanol in carbon tetrachloride.

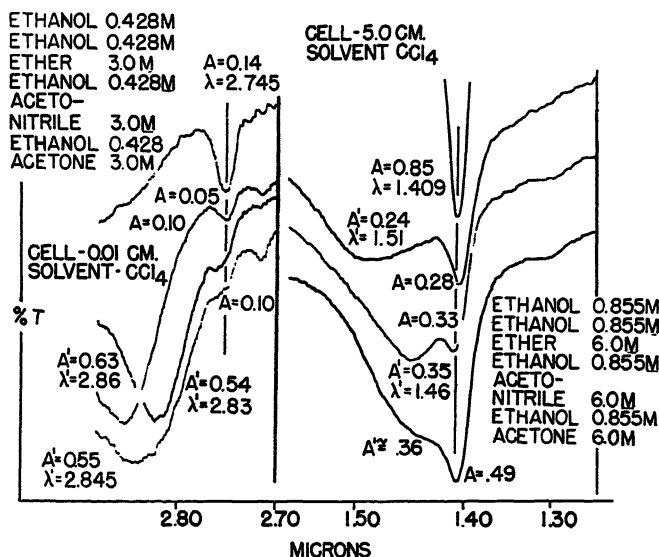


Fig. 2. Fundamental and first overtone spectra of OH stretching vibration of solutions of ethanol in Lewis base solvents.

tained because of its weak intensity. When sufficiently diluted, the associated band disappears, leaving only the sharp "free" band. It may also be observed that the "free" overtone band is more intense relative to neighboring background absorption than is the "free" fundamental band.

Figure 2 shows the effect of adding a small amount of a Lewis base to the ethanol. All of the solutions have been diluted in carbon tetrachloride to minimize the association of alcohol molecules with each other. Again it should be pointed out that the "free" OH band is relatively more intense in the overtone region while the associated band is more intense in the fundamental region. The strength of the bond may be deduced from the perturbation or shift of the OH band upon association. An even more elegant method of determining the bond strength involves measuring the change in concentration of associated molecules as the temperature of the solution is increased.

Another and only recently recognized intermolecular effect which may be studied by means of infrared spectroscopy involves

the weaker electrostatic interactions that always accompany (or better are responsible for) solvation. If one measures the exact wavelength of a solute band center in various solvents the wavelength will be observed to vary slightly. Of course, the bands may be so broad that the band center may be difficult to determine with sufficient accuracy. Fortunately, the overtone bands are often inherently narrower than the fundamental bands thus favoring the near infrared region for this type of study. Figure 3 shows the first overtone of the CH stretching vibration of acetylene in the gaseous state and in several solvents. The small perturbations visible here have in the past been ascribed to the refractive index or dielectric constant of the solvent. However, a careful study reveals no correlation here. Actually, these physical attributes of the solvent are gross effects of the entire solvent molecule and do not reflect the actual electrostatic fields that exist in the immediate vicinity of the solvent molecule. The solute molecule is in this immediate vicinity and is influenced by the solvent fields.

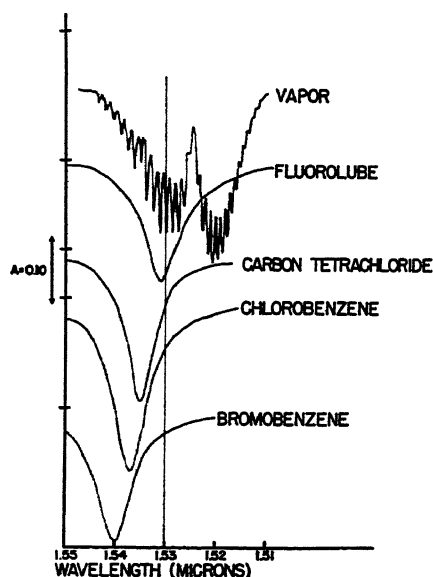


Fig. 3. First overtone of the CH stretching vibration of acetylene as vapor and in solution.

Of course, these electrostatic fields arise from several different factors commonly associated with van der Waal's forces, namely, induction, dispersion, and dipolar forces. However, it is not necessary (or possible at this point) to belabor the source of these forces in order to improve the existing knowledge about intermolecular forces. The dipolar forces predominate and one can summarize by saying that the magnitude of the individual diatomic dipole moments and the distance separating the solute and solvent dipoles largely determine the extent of the interaction. The perturbation increases with the size of the solvent dipoles as evidenced by the effect of the atomic weight of the halogen in the series of halogenated mono-substituted benzenes. Furthermore, the homogeneity of these fields determines the width of the absorption band. A solvent containing only one type of dipole such as carbon tetrachloride will produce the narrowest solute band while a solvent such as 1-chlorodecane will produce a broad solute band.

One can carry spectral observations further and note that solvents disassociate hy-

drogen bonded solute molecules in proportion to the magnitude of the solute-solvent interaction as evidenced by the perturbation of the solute bands. Table 1 tabulates equilibrium constants for *n*-amyl alcohol in several non-hydrogen bonding solvents along with some derived thermodynamic constants and the perturbation of the OH band. Actually, the perturbation is proportional to the heat of association of the alcohol and the heat of association is not solely determined by the equilibrium constant because of the entropy effect. Furthermore, increasing the temperature of the solution results in an expansion or volume increase which inevitably means an increased separation between solute and solvent dipoles. The perturbation of solute bands decreases with increasing temperature by the fifth or sixth power of the intermolecular separation in agreement with theoretical van der Waal's forces. One further distinction should be made here. The author does not consider the hydrogen bond to be a purely electrostatic interaction. The hydrogen bond appears to be a unique form of coordinate linkage. The bond is directional and specifically forms between OH and electron donating (Lewis base) atoms. On the contrary, purely electrostatic interactions occur between any two neighboring dipoles. Proof of the above theory is lengthy and cannot be attempted here, but it does lead to interesting observations on cellulose acetate solutions.

Partially acetylated cellulose (10% resid-

TABLE 1. THERMODYNAMIC DATA FOR *N*-AMYL ALCOHOL WITH LEWIS BASES

Added Compound	K (25°C)	ΔF° (25°), kcal/ Mole	ΔE° kcal/ Mole	ΔV_p cm. ³
amyl alcohol	0.70	-0.21	-4.0	105
ethyl ether	0.81	-0.13	-3.4	155
acetonitrile	0.85	-0.09	-3.6	80
acetone	1.34	-0.17	-2.6	125
pyridine	2.50	-0.54	-4.6	295
dimethylformamide	4.02	-0.83	-3.6	155
dimethyl sulfoxide	9.9	-1.36	-4.0	205

ual OH) dissolves in a number of solvents. Acetone and *s*-tetrachloroethane have been chosen as examples of two entirely different types of solvent. Acetone solvates the cellulose acetate by forming a moderately strong hydrogen bond between the residual OH groups and the carbonyl groups of the acetone. *S*-tetrachloroethane does not hydrogen bond to cellulose acetate but acts as a solvent because of its strong disassociating ability and the electrostatic attraction of CCl dipoles to all of the dipoles of the cellulose acetate molecule. Because of the restrictions of size and polarity, there are few solvents of cellulose acetate that act in the manner of *s*-tetrachloroethane. However, there are considerably more solvents in the hydrogen bonding category. In general, the stronger the hydrogen bond formed the better the solvent, although steric and entropy effects also influence solvation.

The viscosity of cellulose acetate solutions depend to a large extent on these hydrogen bonds. Of course, the major factor governing viscosity is the size of the solute particle. Two solute molecules associated through a hydrogen bond form a solute particle which is obviously larger than the individual unassociated particles. Similarly, the cellulose acetate molecule in associating with solvent molecules by means of hydrogen bonds becomes larger by the number and the size of appended solvent molecules.

We are now in a position to analyze the results of a few cellulose acetate solutions. Table 2 presents the spectral data measured on *n*-amyl alcohol, cellulose acetate (10% residual OH) and water in *s*-tetrachloroethane and acetone. If the assumption is made that the unperturbed OH band of the cellulose acetate occurs at the same wavelength as the OH band of *n*-amyl alcohol vapor, the perturbation of the OH band in the solvents is the same for both solutes. Since the band centers occur at very nearly the same wavelength, it appears logical to assume that the OH groups in these two

TABLE 2. SPECTRAL DATA ON CELLULOSE ACETATE

Solute	Solvent	μ	Breadth (μ)
cellulose acetate	<i>s</i> -tetrachloroethane	1.425	0.065
cellulose acetate	acetone	1.450	0.080
<i>n</i> -amyl alcohol	<i>s</i> -tetrachloroethane	1.426	0.0135
<i>n</i> -amyl alcohol	acetone	1.450	0.060
<i>n</i> -amyl alcohol	vapor	1.3925	0.013
water	<i>s</i> -tetrachloroethane	1.402	0.014
water	acetone	1.416	0.035

widely different molecules behave alike. If this is true, the OH groups in cellulose acetate must not be intramolecularly hydrogen bonded.

Examination of the breadth of the bands reveals considerable difference between these two solutes. The cellulose acetate solution in *s*-tetrachloroethane shows a much broader OH band than *n*-amyl alcohol. The exact reason for this is not clear. The absorption band of the cellulose acetate in *s*-tetrachloroethane is unsymmetrical and this may be indicative of a non-random orientation of solvent dipoles about the OH groups or more likely a variation in the perturbation of different hydroxyl groups. The residual hydroxyl groups are both primary and secondary and the solvent fields may interact differently with the type of hydroxyl group. Studies have indicated slight variations in wavelength of bands from these two types of hydroxy groups.⁴

The wavelength and band width of water in the two solvents have been included in Table 2 in order to make certain that the OH band of traces of water would not be mistaken for the OH band of cellulose acetate. When reasonable efforts were made to reduce the water content of the solvents and solutes and the solvent from the same container was used in the reference path of the spectrophotometer as in the sample path, no difficulty was experienced in interpreting the spectra.

Previous studies have shown that all of the OH groups in solid cellulose and cellulose acetate are hydrogen bonded.^{4, 5} The present study shows that many if not most of the OH bands of partly substituted cellulose acetate in solution in s-tetrachloroethane are "free." There is only a small increase in the absorptivity of the 1.425 μ band on changing the solution concentration from 5 to 2.5% indicating nearly complete disassociation at the lower concentration. However, there is sufficient association to materially affect the solution viscosity. In fact, the solution viscosity is one of the most obvious differences between the acetone and s-tetrachloroethane solutions. In the former, all the inter-cellulose hydrogen bonds are broken and replaced by solvent-solute bonds. In the s-tetrachloroethane solvent, mass action laws predict enough inter-cellulose hydrogen bonds (at 5% concentration) to drastically increase the viscosity of the solutions. Films and fibers prepared from these two solutions are likely to be considerably different. In the non-hydrogen bonding solvents such as s-tetrachloroethane, the cellulose acetate molecules associate with each other through hydrogen bonds to the maximum extent as the solvent volatilizes. In the hydrogen bonding solvents such as acetone, the intercellulose hydrogen bonds do not have a chance to form until the solvent concentration drops to the point where viscosity inhibits orientation of the cellulose acetate molecules for maximum inter-chain hydrogen bonding.

The breadth of absorption bands must be taken into consideration when performing quantitative analysis by means of infrared spectroscopy. The integrated absorptivity of electrostatically perturbed bands does not vary appreciably with the breadth or perturbation of the band. However, the peak absorptivity will vary considerably. It is not usually possible to use the same peak absorptivity values for different solvents.

REFERENCES

1. KAYE, WILBUR, *Spectrochim. Acta* 7, 181-204, (1955).

2. KAYE, WILBUR, *Spectrochim. Acta*, 6, 257-287 (1954).
3. BADGER, R. M., *J. Chem. Phys.*, 8, 288-289 (1940).
4. BROWN, L., HOLLIDAY, P., AND TROTTER, J. F., *J. Chem. Soc.*, 1951, 1532-39.
5. MARRINAN, H. J., & MANN, J., *J. App. Chem.*, 4, 204-211 (1954).

WILBUR I. KAYE

COAL, INFRARED AND ULTRAVIOLET-VISIBLE

Infrared spectra of coal can detect the presence of chemical groups, preclude the existence of suspected structures, and demonstrate similarities of the structure of coal and other carbonaceous materials.^{1, 2} The preferred medium for determining spectra of coal is the petrographic thin section, but the applicability of this method is limited. KBr pellets of coal are universally applicable and are commonly used in most laboratories. Mineral oil and other mulling agents are not too satisfactory, because infrared bands of coal are broad and interference of the bands of the mulling agent is serious.²⁻⁴

The spectrum of vitrain (the principal petrographic component) from Pittsburgh high volatile A bituminous coal, 84% carbon, is given in Figure 1. The principal absorption bands and their assignments are included in the Figure. Spectra were determined through the potassium bromide region to 25 microns, but no bands were found beyond 13.3 microns. The following band assignments are controversial. (1) The strongest band, 6.2 microns, is attributable to either strongly hydrogen-bonded conjugated carbonyl structures, as in β -diketones, or *o*-hydroxyquinones, or aromatic C=C absorption. Preparation of a char of a hydrocarbon with and without the presence of oxygen has shown that an intense 6.2 band occurs only if oxygen is present during the charring process, which indicates that an oxygenated structure of some type is responsible.³ (2) The 6.9 band is due partly to naphthenic CH groups and partly to some other strongly absorbing constituent, pos-

sibly a small amount of inorganic carbonate or a benzenoid group. (3) Absorption at 9.7 microns varies considerably with the ash content of the coal and has been attributed to absorption by minerals of the kaolinite type. (4) The three bands at long wavelength, the so-called aromatic bands, may be due to benzenoid structures, to polynuclear aromatics, or possibly to unsaturated groups. The likely kinds of substitution on aromatic rings are 1,2-, 1,2,4-, 1,2,3,4-, 1,2,4,5- and penta-substitution.

Absorption for Pittsburgh vitrain becomes very strong at the edge of the visible spectrum, at 0.8 micron. This wavelength corresponds to an energy gap for this vitrain of about 1.5 electron volts.⁴

The infrared spectra of chars of various materials are similar to those of coal. In order to produce a coal-like char the material to be charred must have at least one OH group per three carbon atoms, or must be charred in an O₂ atmosphere. The spectra of chars prepared at higher temperatures are

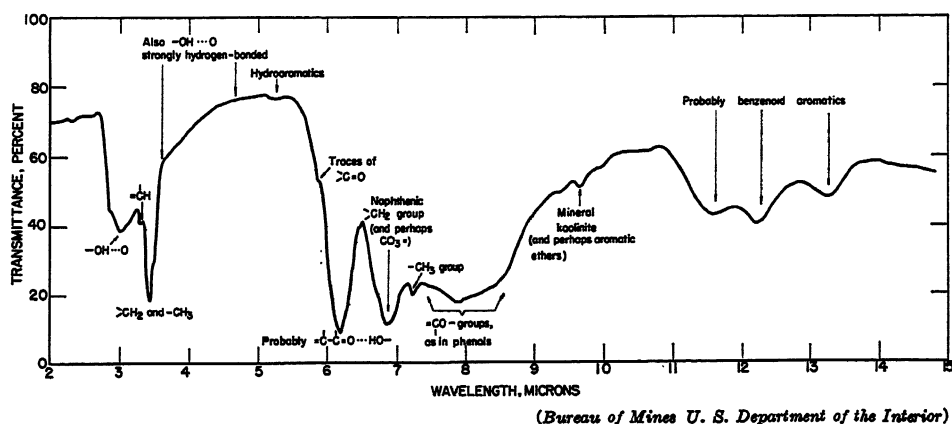


FIG. 1. Infrared spectrum of Pittsburgh vitrain; 0.02 mm section, showing the most probable band assignments.

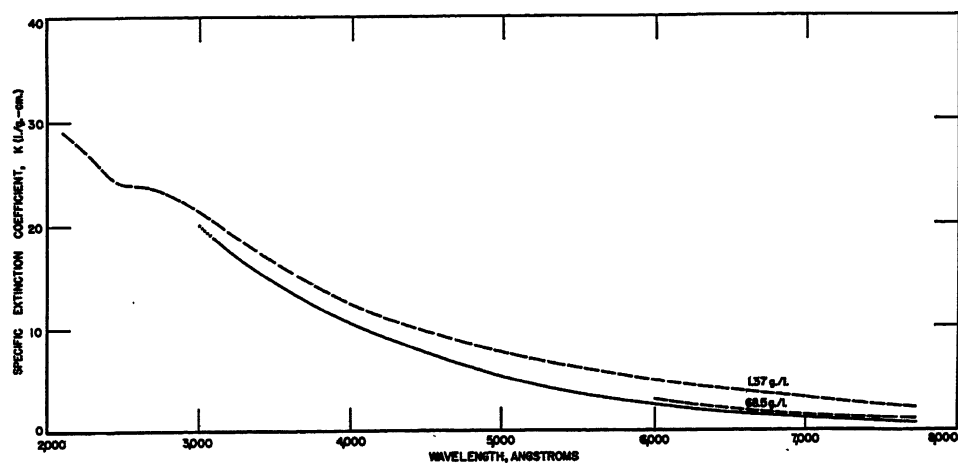


FIG. 2. Ultraviolet-visible spectra of Pittsburgh vitrain; —, thin section and ---, KBr pellets at two concentrations; the higher concentration is preferable because of less scattering loss.

INFRARED SPECTROPHOTOMETRY

TABLE 1. INTENSITIES OF PRINCIPAL ABSORPTION BANDS OF VARIOUS POLYNUCLEAR CONDENSED AROMATICS AND OF CONJUGATED POLYENES. COMPARISON WITH INTENSITIES OF BITUMINOUS VITRAIN

	λ in Å	Specific extinction coefficient, 1/g cm
Coal: Pittsburgh vitrain	2220	28
	3000	20
	4000	10
	5000	5.2
Compound:		
Naphthalene	2220	813
Anthracene	2538	1230
Phenanthrene	2520	416
Pyrene	2400	443
1,2'-Dinaphthyl	2190	512
Chrysene	2670	670
Triphenylene	2570	696
Naphthacene	2740	1640
Coronene	3018	804
Anthanthrene	4330	303
Violanthrene	4920	209
Octatrienol	2650	736
Decatetraenol	2990, 3110	617

similar to the spectra of coals of higher rank. This similarity of spectra of chars and coal has been utilized in assigning structures to various groups in the infrared spectrum.

The charring of coals at several temperatures also has been used to determine the behavior of functional groups. The effect on coal of oxidation, reduction,⁵ functional group reactions, irradiation by neutrons,⁶ gamma rays, electrons, light, etc., can be studied effectively by examination of infrared spectra.

Ultraviolet-visible spectra of coal are most non-specific (Figure 2). There is no fine structure in the spectrum other than the very broad band at about 2650 Å. Little or nothing in the way of identification of chemical constituents can be made from this structureless spectrum. However, the spectrum is usable as a limiting measure of the aromaticity of coal. Physical and chemical evidence in the past have indicated that coal is a substance principally consisting of poly-

nuclear condensed aromatic structures. These materials are extremely intense absorbers of ultraviolet-visible radiation, but a comparison of specific extinction coefficients (K in 1/g cm) in Table 1 indicates that the intensity of absorption shown by the ultraviolet-visible spectrum of a thin section of 84% carbon coal vitrain is not nearly as great as the intensity of absorption of the polynuclear aromatics, or of conjugated polyenes. Analyses based on these data show very low possible concentrations of these compounds in coal.

A more realistic evaluation of possible

TABLE 2. ABSORPTION AREAS UNDER ULTRAVIOLET-VISIBLE SPECTRA OF SOLUTIONS OF POLYNUCLEAR CONDENSED AROMATIC COMPOUNDS; CALCULATION OF MAXIMUM ALLOWABLE CONCENTRATION IN COAL VITRAIN FROM THE ABSORPTION AREAS (UNCORRECTED)

Compound	Absorption area, $\int K \cdot d\lambda$ in liter/g cm ²	Maximum possible concentrations in 84% C vitrain, max wt %
Coal vitrain, 84% C	0.00235 ^a	
Naphthalene	.0102	23
Tetradecahydrocoronene ^b	.0120	20
1,2'-Dinaphthyl	.0110	21
2-(1'-Naphthyl)-1-naphthol ^b	.0103	23
Anthracene	.0113	21
Phenanthrene	.0088	27
1,4-Chrysenequinone ^b	.0084	28
Pyrene	.0076	31
Chrysene	.0097	24
6-Hydroxychrysene ^b	.0094	25
1,2-Benzanthracene	.0090	26
Naphthacene	.0095	25
1,2,5,6-Dibenzofluorene	.0082	29
Coronene	.0083	28
Dicoronyl ^b	.0093	25
Violanthrene	.0099	24
16-Component mixture, equal weights		Ave: 25 25

^a Uncorrected for reflection losses, light scattering by vitrain, or absorption by benzenoid structures, non-aromatics and free radicals.

^b Aromatic nucleus is the same as in the preceding compound.

condensed polynuclear aromatic contents is given by comparing areas under the coal spectra with areas under the spectra of various polynuclear compounds. Results of this comparison are given in Table 2. Possible contents of polynuclear condensed aromatics given in the Table are calculated on the basis that all the absorption under the curve is due to the coal. The value of 25 per cent is a maximum value and indicates that the estimates of high polynuclear aromaticity by other methods are questionable.

The broad absorption band at 2650 Å may be attributable to an unknown carbonyl structure. Absorption in this region is intense for chelated structures such as β -diketones. It is possible that a carbonyl structure might also be responsible for the strongest infrared band, at 6.2 microns.

The color of coal has been attributed by other workers to the high content of polynuclear condensed aromatics. If such structures are not present in large amounts, it is possible that free radicals produce the color. Free radicals are known to be present in coals,^{7, 8} and it has been shown that a simple correlation exists between the intensity of ultraviolet absorption and the free-radical content for untreated coals, coal asphaltene in solvents,⁹ and chemically treated coals.^{2, 3, 4}

REFERENCES

1. BROWN, J. K. *J. Chem. Soc.*, **1955**, 744.
2. FRIEDEL, R. A., AND QUEISER, J. A., *Anal. Chem.*, **28**, 22 (1956).
3. FRIEDEL, R. A., "Proceedings of the Fourth Conference on Carbon," Pergamon Press, to be published.
4. FRIEDEL, R. A., *Fuel*, **38**, 541 (1959).
5. REGGEL, L., RAYMOND, R., FRIEDMAN, S., FRIEDEL, R. A., AND WENDER, I., *Fuel*, **37**, 126 (1958).
6. FRIEDEL, R. A., AND BREGER, I., *Science*, **130**, 3391 (1959).
7. INGRAM, D. J. E., AND TAPLEY, J. G., *Nature*, **174**, 797 (1954).
8. UEBERSFELD, J., ETIENNE, A., AND COMBRISON, J., *Nature*, **174**, 614 (1954).

9. FRIEDEL, R. A., *J. Chem. Physics*, **31**, 280 (1959).

R. A. FRIEDEL

COBLENTZ SOCIETY, INC.

The Coblenz Society was founded in 1954 by a number of leading spectroscopists who realized that a society devoted to the needs of all spectroscopists was very much desired. Named after William W. Coblenz, retired Chief of the Radiometry Section of the National Bureau of Standards, and pioneer in infrared and its applications, the Coblenz Society provides a communications center and voice for the thousands of industrial chemists, scientists, research workers and teachers who use the tools of molecular spectroscopy.

The Society was legally incorporated on December 24, 1958, in Norwalk, Connecticut, as the Coblenz Society, Inc. The principal office is located in Norwalk, in care of The Perkin-Elmer Corporation.

One of the first problems tackled by the Coblenz Society was that of finding a method for the publication of written infrared analytical data. The editors of *Analytical Chemistry* were most cooperative in providing a solution to this problem, and this quantitative infrared data have now become a regular part of each issue of *Analytical Chemistry*.

A well organized program for collecting and publishing infrared spectra of pure compounds has been set up and any individual may contribute to this program by submitting spectra of pure compounds to The Coblenz Society Committee on Infrared Absorption Spectra.

CLARA D. SMITH

DIFFERENTIAL SPECTROSCOPY

Shortly after the appearance of commercial double beam instruments, infrared spectroscopists became aware of the possibilities of

differential spectroscopy.^{2, 5, 6} Infrared differential spectroscopy permits one to obtain the spectrum of a minor component of a mixture in solution. The technique is simply an extension of the well known solvent compensation method.

The technique of solvent compensation utilizes the double beam principle in compensating or cancelling out solvent absorption by placing an equivalent amount of solvent in the reference beam. The resulting spectrum contains only solute absorption bands. In differential spectroscopy, a solution containing both a major and minor component is placed in the sample beam. An equivalent amount of solvent and major component are placed in the reference beam. The resulting spectrum then contains only minor component absorption bands.

It can be seen at once that this technique affords greatly increased sensitivity both for qualitative and quantitative studies of trace components.

In qualitative studies of a mixture, the overlapping of infrared absorption bands by the major component often makes difficult, and sometimes prevents, the detection of the minor components. The differential technique of double beam infrared spectrometry has largely overcome this limitation, and has proved most successful in detecting and identifying minor components.^{1, 4}

Infrared differential spectroscopy is also used to advantage in the quantitative determination of minor components because of two important factors. One of these factors is the elimination of overlapping absorption of the major absorber. The other factor is the "blowing up" of the instrument ordinate scale that this technique effects. This increase in sensitivity will permit quantitative analyses of trace components in the range of 0.1 to 1.0% with a precision of about $\pm 0.01\%$ when an inherently strong absorption band is employed.⁷

The method is also being used in the following way as a criterion of purity: Equal

weights of pure standard and sample are separately dissolved in equal volumes of an appropriate solvent and placed in matched cells. If the resulting spectrum is essentially a straight line, the pure standard and sample are identical.³

Another interesting application of differential spectroscopy has been in the study of overlapping bands in pure compounds of unknown structure. When it is suspected that one broad band represents partial superimposing of two functional group absorptions, one of the absorptions may be cancelled by placing a different material in the reference beam which contains an equivalent amount of one of the suspected functional group absorptions.

For optimum results in obtaining differential spectra, a few special conditions should be observed. Among these are several instrumental adjustments aimed at compensating for the large losses in energy involved. These measures include adjusting the source to full intensity, increasing the slit widths, and increasing the electronic gain. In addition, when choosing concentration and cell thickness, it should be noted that whenever more than 95% of the incident radiation is absorbed, the instrument is effectively inactive. Absorption cells should be clean and well matched.

The differential technique in itself has enabled infrared spectroscopists to increase the sensitivity of quantitative determinations by at least a factor of 10. Keeping pace with this development, there have been two significant instrumental improvements which implement differential analysis. These are known as automatic gain control and ordinate scale expansion. Automatic gain control provides a constant gain over a transmission range of 10 to 100% and thus ensures a live pen under minimum energy conditions. The ordinate scale expansion feature, with some loss in resolution, will permit up to a twentyfold expansion of any portion

of the ordinate. With minimal loss in resolution a tenfold expansion may be achieved.

Further sharpening of the differential technique will certainly be realized with improvements in spectrometer sources, detectors, and monochromators.

REFERENCES

1. CLARK, W. H., *Anal. Chem.*, **31**, 197 (1959).
2. HAMMER, C. F., AND ROE, H. R., *Ibid.*, **25**, 668 (1953).
3. McDONALD, I. R. C., *Nature*, **174**, 703 (1954).
4. POWELL, H., *J. Appl. Chem.*, **6**, 488 (1956).
5. ROBINSON, D. Z., *Anal. Chem.*, **23**, 273 (1951).
6. ROBINSON, D. Z., *Ibid.*, **24**, 619 (1952).
7. WASHBURN, W. H., AND SCHESKE, F. A., *Ibid.*, **29**, 346 (1957).

W. H. WASHBURN

EQUILIBRIUM CONSTANTS OF COMPLEX METAL IONS

In 1950, Hunt *et al.*,⁵ examined the infrared spectra of various minerals in the solid state. In order to obtain spectra free from interference of Nujol and fluorolube, these workers examined solids which had been ground to a particle size of less than 5 μ in diameter. The finely ground material was then spread as a thin layer on sodium chloride windows. Miller and Wilkins¹¹ published in 1952 the infrared absorption spectra of 159 inorganic compounds. Nujol and fluorolube were used to mull most of the crushed solids. Among the compounds studied was potassium ferricyanide, which has a characteristic absorption band at 2100 cm^{-1} . Three ferrocyanides, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10 \text{H}_2\text{O}$, $\text{Ca}_2\text{Fe}(\text{CN})_6 \cdot 12 \text{H}_2\text{O}$, and $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O}$, were also examined and found to have a characteristic absorption band at about 2010 cm^{-1} . Absorption at this wave number is caused by carbon-nitrogen stretching of the $\text{C}\equiv\text{N}$ group, which as an uncomplexed ion absorbs at 2070–2080 cm^{-1} . Jones and Penneman⁷ state that the peaks observed for cuprous cyanide complexes are also caused by a similar stretching.

In 1954, Jones and Penneman⁶ conducted

an infrared study of aqueous solutions of AgCN-KCN . A solution containing three complex species was made by adjustment of the relative concentrations of silver ion and cyanide ion. Spectra of solutions containing only the $\text{Ag}(\text{CN})_2^-$ complex were found to follow Beer's Law and were used to determine the molar absorptivity of this species. Known amounts of cyanide ion were added to change the ratio of $\text{Ag}(\text{CN})_2^-$ to $\text{Ag}(\text{CN})_3^-$. Simultaneous equations were set up and the molar absorptivities for each species determined. The concentration of these two species was calculated from the molar absorptivities and the absorbance of each species. The concentration of $\text{Ag}(\text{CN})_4^-$ was found by the difference between the stoichiometric amount of $\text{Ag}(\text{I})$ and the concentrations of the other complexes. From these data the following equilibrium constants were determined:



$$K = 0.108 \text{ mole l}^{-1}$$



$$K = 2.85 \text{ mole l}^{-1}$$

In a later paper Jones and Penneman⁷ applied the same methods to an investigation of aqueous solutions of CuCN-KCN and CuCN-NaCN systems. Spectra of solutions containing only $\text{Cu}(\text{CN})_4^-$ obey Beer's Law and were used to calculate the molar absorptivity of this species. The molar absorptivity for $\text{Cu}(\text{CN})_3^-$ was determined by changing the ratio of $\text{Cu}(\text{CN})_4^-$ to $\text{Cu}(\text{CN})_3^-$ by addition of $\text{Cu}(\text{CN})_2^-$ and solving simultaneous equations. The concentration of $\text{Cu}(\text{CN})_2^-$ after reaction was found by the difference between the concentrations of $\text{Cu}(\text{CN})_3^-$ and $\text{Cu}(\text{CN})_4^-$ and the total $\text{Cu}(\text{I})$ concentration. Using these data the following ionization constants were determined:



$$K = 1.5 \times 10^{-8} \text{ mole l}^{-1}$$

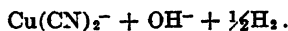
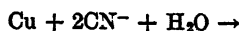


$$K = 5.7 \times 10^{-8} \text{ mole l}^{-1}$$

INFRARED SPECTROPHOTOMETRY

The measurements were made at 29°C and were corrected to 25°C by the use of ΔF obtained by measuring the absorbance of a solution over a temperature range of 0 to 60°C.

For a complete analysis of the system, the dissociation constant for $\text{Cu}(\text{CN})_2^-$ must be determined. This constant is not easily determined because of the difficulty of measuring the emf of a cell containing a copper electrode in alkaline cyanide. At high pH, the copper electrode dissolves with liberation of hydrogen according to the equation:



In order to obtain reproducible emf measurements for a cell containing a copper electrode in cyanide solution, Vladimirova and Kakovsky¹² used a hydrocyanic acid solution containing excess cuprous cyanide. They assumed that $[\text{H}^+] = [\text{Cu}(\text{CN})_2^-]$. After removal of the excess cuprous cyanide by filtration, the hydrogen ion was determined by direct titration with sodium hydroxide and the concentration of the copper (I) was determined by titration with potassium iodate.⁸ The results substantiated the assumption; thus only the lowest cuprous cyanide complex was present in appreciable amounts.

Calculations of the dissociation constant for $\text{Cu}(\text{CN})_2^-$ involve the dissociation constant of hydrocyanic acid. Because literature values^{1, 2, 3, 4} for the latter constant are not in agreement, uncertainty is introduced in the value for the $\text{Cu}(\text{CN})_2^-$ dissociation constant.

McAlpine¹⁰ estimates the maximum value for the equilibrium constant for the reaction



to be 1.2×10^{-29} at 25°C. Jones and Penneman⁷ calculate this constant to be 2.6×10^{-29} at 25°C from the dissociation constant of $\text{Cu}(\text{CN})_2^-$ and the first ionization constant of $\text{Cu}(\text{CN})_2^-$.

The infrared method for the determina-

tion of dissociation constants of the cuprous cyanide complexes has the advantage that the system may be studied in alkaline solution in the presence of all three complexes. Potentiometric methods cannot be used. Polarographic determinations of these constants are not possible because of the extreme stability of the complex species.⁹

In general this method is limited in that the species must absorb in a range where there is no interference by the absorption bands of water, and the species must obey Beer's Law.

REFERENCES

1. BORNSTEIN, L., "Physikalisch-chemische Tabellen," Vol. II, p. 1126, Springer, Berlin, 1923.
2. BORNSTEIN, L., *ibid.*, Supl. I, p. 648, 1927.
3. BORNSTEIN, L., *ibid.*, Supl. III, Part III, pp. 2108, 2157, 1936.
4. BRITTON, H. T. S., AND DODD, E. N., *J. Chem. Soc.*, **1932**, 2332.
5. HUNT, J. M., WISHERD, M. P., AND BONHAM, L. C., *Anal. Chem.*, **22**, 1478 (1950).
6. JONES, L. H., AND PENNEMAN, R. A., *J. Chem. Phys.*, **22**, 965 (1954).
7. JONES, L. H., AND PENNEMAN, R. A., *ibid.*, **24**, 293 (1956).
8. KOLTHOFF, I. M., AND BELCHER, R., "Volumetric Analysis," p. 470, Interscience, New York, 1957.
9. KOLTHOFF, I. M., AND LINGANE, J. J., "Polarography," Vol. II, pp. 494-495, Interscience, New York, 1952.
10. McALPINE, R. K., *Anal. Chem.*, **25**, 331 (1956).
11. MILLER, F. A., AND WILKINS, C. H., *ibid.*, **24**, (1253 1952).
12. VLADIMIROVA, M. G., AND KAKOVSKY, I. A., *Zhur. Priklad. Khim.*, **23**, 580 (1950).

EDMUND S. BERCHERT, JR.

FATTY ACIDS AND RELATED COMPOUNDS

A survey of the technical literature reveals that until the beginning of the past decade, the fatty acid chemist made very little use of infrared spectroscopy. A review paper published about the middle of the 1950's¹ showed that only a few scattered articles (now mainly of historical interest) dealing with the

application of infrared spectrophotometry to fatty acid derivatives could be found in the literature prior to 1950.

With the start of the '50's, publications describing applications of infrared spectroscopy to fatty acid chemistry began to appear in increasing numbers. During the first half of the decade, from 1950 through 1954, an average of some twenty papers a year appeared, 49 of these in the single year 1954. This interest in the use of infrared spectroscopy by the fatty acid chemist has continued to increase during the second half of the decade. Now at least fifty research papers dealing with applications of infrared absorption spectroscopy to fatty acid chemistry are published annually. A more recent review in German which appeared about the middle of 1958 lists 247 references, about 100 of which were published since the beginning of 1955.²

Most of the applications of infrared absorption spectroscopy by the fatty acid chemist, including techniques for qualitative identifications or for quantitative determinations, or for clues to the molecular structure of fatty acid derivatives, have been based on the empirical "group frequency" approach. Infrared absorption bands arise as a result of changes in vibrational levels of a molecule and the absorption spectrum becomes a "fingerprint" of a specific molecule. The fatty acid chemist, however, when first using this tool had no fingerprint files for identifications by direct comparisons and resorted to "group frequency" analyses.

Julius³ was probably the first to point out that the infrared spectra of all compounds containing a specific group exhibited the same absorption maxima. He showed, for example, that the infrared spectra of compounds containing the methyl group always exhibit a band with maximum at 3.45 microns. Such empirical correlations of vibrating groups with specifically observed absorption maxima suggested the possibility of chemical identification and, coupled with intensity measurements, of quantitative de-

terminations. The research papers appearing in the early 1950's were mainly surveys or investigations of the infrared spectra of fatty acids, esters, glycerides and other derivatives to establish correlations which would be useful to the fatty acid chemist in either research problems or in quality control.⁴ In the review article previously referred to¹, O'Connor has included a table listing "One Hundred Absorption Bands Employed in the Applications of Infrared Spectroscopy to Fatty Acid Chemistry" (Table 1). It was the breakthrough establishing these correlations which ushered in the rapidly increasing application of infrared spectroscopy to fatty acid chemistry.

Most useful correlations have been found either in the "rock salt" region of the spectrum from about 2 to 15 microns or, more recently, in the near infrared region from just above the visible red, *ca.* 800 millimicrons to about 2.5 microns. Measurements in these regions can be used to establish the presence (or absence) of specific functional groups, to identify constituents in the analysis of natural products, or to confirm (or obtain initial clues to) molecular structure. Absorptivities calculated for bands assigned to specific groups can be used, in equations derived from the Bouguer-Beer law, for quantitative analysis of single components or multicomponents in a manner analogous to the use of these expressions in ultraviolet spectrophotometry. The identification and intensities of bands correlated to specific groups can also be used to follow the course of chemical reactions or to determine the rates of these reactions.

The 0.8 to 2.5 Micron Region

While "group frequencies" throughout the infrared spectrum are used in the identification of compounds or the elucidation of molecular structure, several problems involve essentially measurements in specific regions. For convenience, illustrations of the applications of infrared spectroscopy to fat

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TABLE 1. ONE HUNDRED ABSORPTION BANDS EMPLOYED IN THE APPLICATIONS OF INFRARED SPECTROSCOPY TO FATTY ACID CHEMISTRY^a

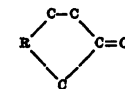
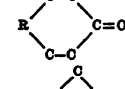
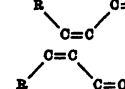
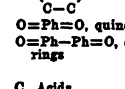
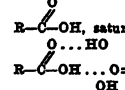
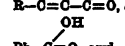
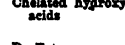
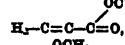
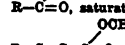
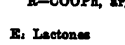
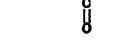
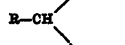
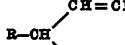
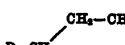
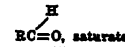
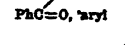
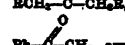
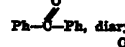
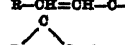
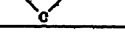
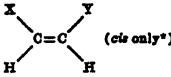
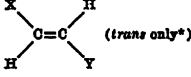
No.	Wavelength position of observed absorption band	Vibrating group giving rise to observed absorption band	No.	Wavelength position of observed absorption band	Vibrating group giving rise to observed absorption band
	microns			microns	
		I. O—H, C—H, N—H, C—D, P—OH, and P—H stretching vibrations. Regions 2 to 5 microns	34	5.73	 C=O, 5-membered, saturated ring
1	2.75-2.80	A. O—H stretching	35	5.81	 C=O, 6-membered, saturated ring, or
2	2.83-2.90	Free O—H			 C=O, 5-membered, α,β unsaturated ring
3	2.95-3.25	Bonded O—H . . . O of single-bridged dimer			 C=O, 6- (or 7-) membered, α,β unsaturated ring
		Bonded H . . . O—H . . . O of double-bridged polymer or cyclic	36	5.95	 C=O, 5-membered, saturated ring
4	3.00-3.05	B. C—H stretching	37	5.90-6.00	O=Ph=O, quinone, 2 C=O's on 1 ring
5	3.22-3.25	R ₃ C—H	38	6.05-6.10	O=Ph—Ph=O, quinone, 2 C=O's on 2 rings
6	3.28-3.32	R ₂ C=O—H ₂			C. Acids
7	3.40-3.45	R ₂ C=O—HR	39	5.68	 R—C(=O)OH, saturated monomer
8	3.42-3.50	R ₂ C—H ₂	40	5.80-5.88	 R—C(=O)OH . . . HO—C(=O)R, saturated dimer
9	3.45-3.48	R ₂ —OH	41	5.90-5.92	 R—C(=C(OH))=O, α,β unsaturated
10	3.50-3.70	R—C(=O)H	42	5.90-5.95	Ph—C(=O)O, aryl
11	3.70	C—H and bonded O—H . . . O combination band	43	6.00-6.05	Chelated hydroxy-acids, some dicarboxylic acids
		C. N—H stretching			D. Esters
12	2.85 and 2.95	Free N—H primary amide	44	5.65	 H ₂ C=C(OCH ₃)=O, vinyl ester
13	3.00 and 3.15	Bonded N—H . . . primary amide	45	5.75	 R—C(=O)OCH ₃ , saturated
14	2.90-2.95	Free N—H secondary amide	46	5.80-5.83	 R—C(=C)C(=O)OCH ₃ , α,β unsaturated, or
15	3.00-3.05	Bonded N—H . . . secondary amide, single bridge (trans)			E. Lactones
16	3.15-3.18	Bonded N—H . . . secondary amide, single bridge (cis)	47	5.50	 O, β, or 4-membered saturated ring
17	3.22-3.35	Bonded N—H . . . secondary amide cyclic dimer	48	5.65	 O, γ, or 5-membered saturated ring
18	2.85 and 3.02	N—H primary amine			 O, γ, or 5 membered α,β unsaturated ring
19	2.85-3.02	N—H secondary amine	49	5.72	 O, ε, or 6-membered saturated ring
20	2.95-3.12	N—H imine			 O, ε, or 6-membered α,β unsaturated ring
21	3.20-3.30	N—H ₂ ⁺ amino acids	50	5.75	 O, ε, or 6-membered saturated ring
		D. C—D stretching			
22	4.64	C—D			
23	4.84	C—D			
		E. P—H, P—OH stretchings			
24	4.05-4.25	P—H			
25	3.70-3.90	P—OH			
		II. C=O and C=C, C≡C stretching vibrations. Region 5.0 to 6.0 microns			
		A. Aldehydes			
26	5.75-5.90	 R—C(=O)H, saturated			
27	5.83-5.90	 Ph—C(=O)H, aryl			
28	5.85-5.95	 R—CH=CH—C(=O)H, α,β unsaturated			
		B. Ketones			
29	5.80-5.85	 RCH ₂ —C(=O)—CH ₂ R, saturated			
30	5.90-5.95	 Ph—C(=O)—CH ₂ R, aryl-alkyl			
31	6.00-6.02	 Ph—C(=O)—Ph, diaryl			
32	6.00-6.05	 R—CH=CH—C(=O)R, α,β unsaturated			
33	5.63	 C=O, 4-membered, saturated ring			

TABLE 1. (continued)

No.	Wavelength position of observed absorption band	Vibrating group giving rise to observed absorption band	No.	Wavelength position of observed absorption band	Vibrating group giving rise to observed absorption band
	microns			microns	
51	6.0-6.1	F. C=O, C≡O stretching C=O <i>cis</i> only (weak when internal in symmetrical molecules)	86	11.90-12.50	
52	3.08	HO≡OH	87	13.0 > 15.0	
53	4.67-4.76	RO≡OH			
54	4.44-4.58	RO≡OR			
55	5.14 and 9.45	C=C=C			
		III. C-H deformations, saturated groups. Region 6 to 7 microns			
56	6.7-6.9	-C-H ₂ - group			
57	6.8-7.0	-C-O-H ₂ group, asymmetrical deformation			
58	7.15-7.20	-C-(C-H ₂) ₂ group			
59	7.30-7.25	-C-(C-H ₂) ₃ group			
60	7.35-7.30	C-O-H ₂ group symmetrical deformation			
61	7.30-7.35	-C-(C-H ₂) ₃ group			
62	7.45-7.50	-C-H- group			
		IV. C-O stretching and C-OH bending. Region 7.7 to 10.0 microns			
		A. Alcohols			
63	7.2-8.6	Phenols	88	9.75 and 11.55	B. Skeletal and "breathing"
64	8.3-8.9	Tertiary open-chain saturated			
65	8.9-9.2	Secondary open-chain saturated	89	10.9 and 11.3	Cyclopropane
66	9.2-9.5	Primary open-chain saturated	90	10.31 and 11.16	Cyclobutane
67	8.3-8.9	Highly asymmetrical-branched secondary	91	9.63, 9.86,	Cyclopentane
68	8.9-9.2	α-Unsaturated or cyclic tertiary		11.05 and 11.60	Cyclohexane
69	9.1-9.2	Secondary with branching on one α-carbon	92	11.2	Epoxy-oxirane ring derived from internal R-C≡C-R (trans only)
70	9.2-9.5	Secondary, α-unsaturated or allylic 5- or 6-membered ring	93	13.0	Epoxy-oxirane ring derived from internal R-C≡C-R (cis only)
71	9.5-10.0	Secondary: di-unsaturated, α-branched and unsaturated, or 7- or 8-membered ring			
		Primary: α-branched and/or unsaturated			
		Tertiary: highly unsaturated			
		B. Acids			
72	7.75-7.80	C-O	94	11.8, 12.9, and 14.7	Benzene ring
73	8.40-8.45	C-O	95	12.0	Hydroperoxide
		C. Esters	96	12.95	Ethyl
74	7.90-8.00	C-O	97	13.0	OH ₂ rocking on long carbon chain
75	8.40-8.50	C-O	98	13.5	n-Propyl
		D. Ethers	99	13.5	Hydroperoxide
76	8.7-9.4	OH ₂ -O-CH ₂ , alkyl	100	7.5-8.5	Progression of bands in solid state spectra, probably due to wagging and/or bending mode of vibration of the O-H bonds of methylene groups. The number of bands in the progression is indicative of chain length.
77	7.8-8.1	Ph-O-Ph, aryl or =C-O, unsaturated			
		E. Anhydrides			
78	7.7-8.3	Cyclic			
79	8.5-9.5	Open chain			
		F. Phosphorus			
80	6.90 and 10.0	P-O-Ph, aromatic			
81	9.52	P-O-OH ₂ aliphatic			
		V. C-H deformation about a C≡C and skeletal and "breathing" vibrations. Region 10.0 to 15.0 microns.			
		A. C-H bending			
82	10.05-10.15				
83	10.20-10.36				
84	10.90-11.05				
85	11.17-11.30				

* The exact position of maximum absorption depends upon whether the measurements were made on the pure liquid, solid, molten, or solvent and on the nature of the particular solvent. Several band positions are also critically dependent upon neighboring groups.

The value and range given in this table are from the author's collection of these bands in fatty acid materials mostly from original reports in technical journals. They represent average values of ranges of the various data that have been reported for the specific absorption.

and oil chemistry will be discussed in selected wavelength regions. Figure 1 shows the infrared absorption spectra of typical fatty acid materials.

The near infrared region of the spectrum is defined roughly as the wavelength interval just above the visible red, about 800 millimicrons, to about 2.5 microns. This region was the first to be investigated by infrared spectroscopists as an extension of the visible region when photographic plates were used as the only detectors with glass or quartz optics. With the advent of thermocouples and bolometers as detectors and the introduction of sodium chloride optics, investigations in the rock salt region, from about 2.5 to 15 microns, were actively pursued and the near infrared region largely neglected. The recent extension of the ultra-

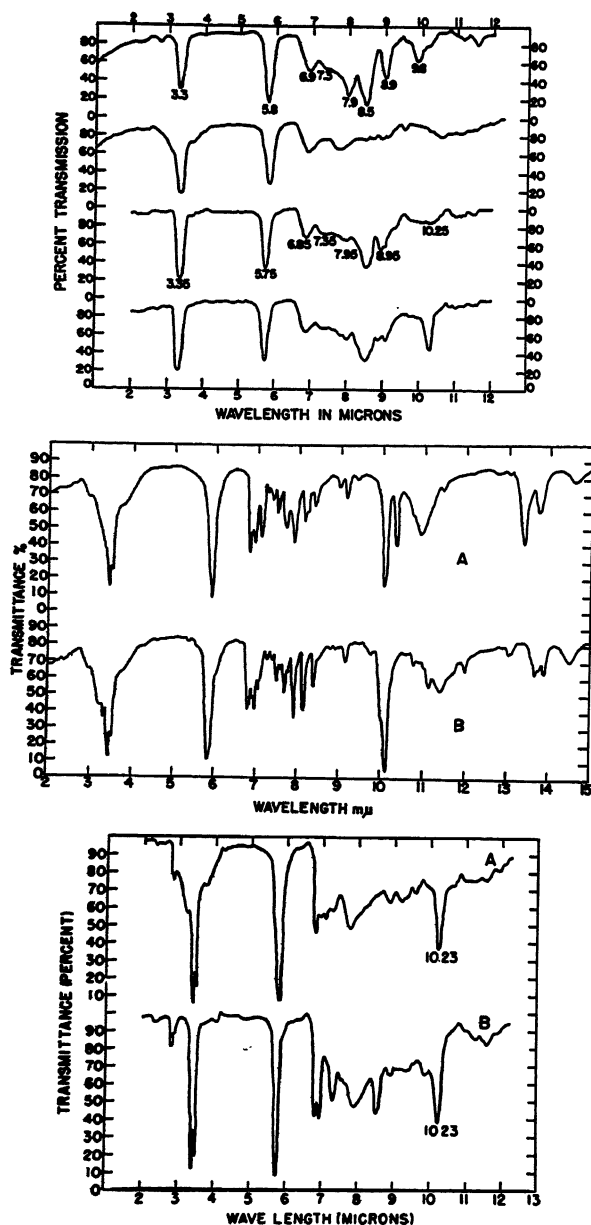


FIG. 1. Infrared absorption spectra of typical fatty acid materials. Stearic acid, methyl laurate, tristearin, trielaidin, ricinelaidic acid, methyl ricinelaidate, alpha-eleostearic acid, beta-eleostearic acid.

violet—visible spectrophotometers to include wavelengths to 2.5 or 3.0 microns has resulted in a revival of interest in this region. In the near infrared region are found many absorption bands resulting from overtone

and combination bands associated with hydrogen atoms. Among these are the first overtones of the —OH and —NH hydrogen stretching vibrations near 1.4 and 1.5 microns, respectively, and combination bands

resulting from C—H stretching and deformation vibrations of alkyl groups at 2.2 and 2.6 microns.

Holman and Edmondson have published a report of a survey of the near infrared region and its potential applications to fatty acid chemistry.⁵ Of particular interest to the lipide chemist, they found that it was possible to distinguish *cis* double bonds, terminal double bonds, hydroxyl groups, amine groups, hydroperoxide and carbonyl and carboxyl compounds. For identification and determination of these groups the near infrared offers, in certain cases, advantages over longer wavelength regions. For example, bands at 1.18, 2.14 and 2.19 microns, which should lend themselves to quantitative analysis, were attributed to *cis* unsaturation. Similar bands in the 10 micron region (which have been used very successfully for determinations of *trans* bonds) have not proved very satisfactory for the direct determination of the *cis* isomers. Furthermore, in the near infrared spectra these measurements of *cis* unsaturation are entirely free from any interference by *trans* isomer vibrations. Similarly, the hydroperoxide group can be easily recognized and measured in the near infrared region by overtone bands at 1.46 and 2.08 microns, whereas the fundamental vibrations about 2.8 microns usually do not distinguish these structures.

Identification and Determination of Unsaturated *Cis* Bonds. Goddu⁶ showed that bands in the near infrared at 1.6 or 2.1 microns could be used to determine quantitatively terminal double bonds in several types of organic molecules with a sensitivity within 0.01% C=CH₂, and that *cis* double bonds could be determined at 2.1 microns with a sensitivity of about 1% —CH=CH—. No methods for *trans* bonds appeared available in the near infrared (see discussion under 10 micron region, p. 430). The absence of absorption attributable to *trans* isomers makes it possible to analyze mixtures containing terminal, *cis* and *trans* double bonds

rapidly and accurately for *cis* and terminal double bond content.

Holman, Ener and Edmondson⁷ investigated the application of near infrared absorption to the analysis of fatty acids and fatty acid derivatives for *cis* isomer content. They found that the method could be employed for rapid analysis of fatty acids, methyl and ethyl esters, triglycerides, cholesterol esters and fatty aldehydes. They compared results for the analysis of these types of materials for *cis* content by the direct near infrared procedure with the calculation by means of a determination of *trans* isomer content (from measurements in the 10 micron region), an estimation of total unsaturation by means of iodine value, and calculation of *cis* content by difference. Results by the direct and indirect methods were in reasonably good agreement. The near infrared procedure as a direct method for *cis* isomer content has the decided advantages of rapidity, selectivity, and sensitivity, which should be of considerable help to the lipide chemist.

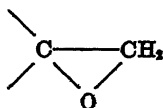
More recently, Fenton and Crisler⁸ have described the determination of *cis* unsaturation in oils by near infrared spectroscopy. They have reported details for the satisfactory application of the method to the analysis of vegetable and drying oils, hydrogenated oils, shortenings and margarines by a differential infrared technique.

Hydroxyl Number and Hydroperoxide Determination From Near Infrared Measurements. Another application of the near infrared which is of considerable interest to the fatty acid chemist is the direct determination of hydroxyl number by measurement of the —OH overtone band intensities. Crisler and Burrill⁹ have described a method for determination of the hydroxyl value of aliphatic primary alcohols from measurement of the hydroxyl-stretching overtone band at 1.4 microns. The procedure was compared to the chemical acetic anhydride—pyridine method. Comparison of the

near-infrared and chemical procedures, calculated as a standard deviation, was 0.27, which is better than the standard deviation of the chemical method, 0.77, for hydroxyl value determinations in the same range. Attempts to extend the method to the determination of hydroxyl values of secondary, tertiary, branched alcohols and to phenolic compounds showed conclusively that there is a relatively wide variation in absorptivities of the various types of alcohols and that a single calibration curve cannot be used for all —OH containing systems. The near-infrared procedure can be used for any system after suitable calibration data are obtained.

C. L. Hilton¹⁰ used near-infrared bands between 2.0 and 3.0 microns to determine the hydroxyl numbers of polyesters and polyethers. Interferences by acids, alcohols, hydroperoxides, and other —OH containing compounds and from amides, amines and oxamines were corrected mathematically.

Upon examination of the near-infrared spectra of a number of hydroperoxides of fatty acid esters and related substances, Holman and co-workers¹¹ found that only those compounds having an —O—O—H group exhibited absorption bands at 1.46 and 2.07 microns. These bands were used to follow the thermal decomposition of the methyl oleate hydroperoxide and the autooxidation of methyl linoleate. Intensities of the bands at 1.46 and 2.07 microns were shown in both studies to parallel the iodometric peroxide values. Terminal epoxides have sharp absorption bands in the near-infrared region at 1.65 and 2.20 microns. These bands were used by Goddu and Delker¹² for the quantitative determination of the epoxide ring in the range of 10 gamma per ml of



with an accuracy and precision over most of

this range of from ± 1 to 2 % of the amount present.

The 3 Micron Region

Investigations of Oxidation and Auto-oxidation. Several workers have used the —OH stretching fundamental band at about 2.8 microns to obtain further understanding of the complex problems of autooxidation and rancidity—problems of considerable importance to the lipide chemist. (References to the original publications will be found in the review article cited above.¹) Dugan, Beadle and Henick examined the infrared spectra of autooxidized methyl linoleate. In the region of —OH stretching, 2.8 to 3.0 microns, two bands were observed both increasing with increased peroxide value, one sharp and distinct at 2.88 microns, the other broad with maximum about 2.92 microns. Reduction of the oxidized sample with KI resulted in the disappearance of the band with maximum at 2.92 microns and appearance of a new band with maximum at 2.86 microns. The band with maximum at 2.92 microns was attributed to the hydroperoxide, —O—O—H, group associated by hydrogen bonding. The bands at 2.86 and 2.88 microns were attributed to the —OH stretching vibrations. These conclusions differ from those of Shreve *et al.*, who considered the hydroperoxide and hydroxyl stretching vibrations to be identical. However, only under conditions of highest resolution would the differences reported by Dugan, Beadle and Henick be observed. Now, after ten years development of infrared spectroscopy since the report of Dugan, Beadle and Henick, it might be of interest to investigate these oxidation products in the near infrared, observing changes in the overtone region, where hydroxyl, hydroperoxide, aldehyde, etc., groups appear to be well resolved and readily recognized.⁵

Early in the last decade, Lemon, Kirby and Knapp examined fractionated products of methyl esters of peanut oil fatty acids

autooxidized at temperatures of 22 to 100°, by means of infrared spectra. In the region of —OH stretching vibration they found a band developing in the early stages of auto-oxidation which they believed to be associated with the hydroperoxide —O—O—H group. Later two bands at longer wavelengths appeared which were attributed to decomposition of the hydroperoxide to other compounds containing —OH groups. Increasing the temperature increased the rate of both hydroperoxide formation and decomposition. The presence of iron stearate catalyzed only the decomposition.

Catravas and Krafo found, from examination of infrared spectra, that autooxidation of methyl oleate and methyl linoleate gave unstable alcohols which are subsequently further oxidized to ketones. The —OH stretching band at 2.9 microns was used by Honn, Bezman and Daubert to study the autooxidation of linseed oil. A nonuniform increase in the intensity of this band is noted, very slow during an initial induction period, then very rapid as the various oxidation reactions proceed at accelerated pace. The increase in the intensity of the 2.9 micron band during autooxidation was accounted for by formation of hydroperoxide —O—O—H, carboxyl, —COOH, and alcohol or water ROH groups, all giving rise to —OH stretchings. By a combination of chemical and spectrophotometric methods, the increase in concentration of each of these groups was followed.

The peracetic and performic acid oxidation of linoleic acid was studied by McKay, Levitin and Jones. Two new oxidation products were isolated along with the isomeric sativic acids. These were partially characterized by means of infrared absorption spectroscopy. Spectra established that the compound formed by oxidation with performic acid contained hydroxy groups in the chain. A weak band at about 3.27 microns indicated either an unsaturated linkage or possibly a cyclopropyl group. The latter appears more

probable since the spectra failed to show any evidence of unsaturation at either the region of C=C stretching, about 6.0 to 6.2 microns, or in the region of C—H bending, about the C=C group, between 10 and 11 microns.

Smith, Freeman and Jack obtained infrared absorption curves of monoethenoid methyl ester fractions of milk fat in the range C₁₀ to C₂₀ and compared them to available spectra of pure saturated and unsaturated esters of long chain fatty acids. Absence of a band at 2.8 to 2.9 microns showed that no oxidation had occurred to give hydroperoxidic hydroxyl formation. Methyl linoleate hydroperoxide, produced by ultraviolet catalyzed oxidation of methyl linoleate, was thermally decomposed in the presence of the methyl linoleate by Williamson. The thermal decomposition products, consisting of monomers, dimers, and trimers, were studied by means of infrared absorption spectra.

Studies of Drying Oil Mechanism. Another problem in which infrared absorption spectroscopy has been proving to be of considerable help to the fatty acid chemist is that of the drying mechanism of drying oils. Adams and Auxier reported changes in the infrared spectra of synthetic oils as a function of drying time. The intensities of a band at about 2.8 microns, attributed to formation of the hydroperoxide group, and of a band at 3.27 microns, assigned to a C—H stretching on a carbon atom adjacent to a double bond, were followed as drying proceeded. The 2.8 micron band increases in intensity and the 3.27 band decreases until finally a reasonably stable value is reached by each at about the same time. This is the effect to be expected if one band represents increase in hydroperoxide formation and the other decrease in unsaturation during drying process. Slopes of curves of intensity versus drying time were of the same order as drying rates. Linolenates had steeper slopes than linoleates, which were in turn steeper than oleates, again in agreement with known dry-

ing rates. This was interpreted as support for the theory that the carbon atom alpha to a double bond is particularly susceptible to oxidation and that a methylene carbon between two double bonds is more so.

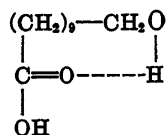
Adams, Auxier and Wilson interpreted results of their studies of the infrared absorption of dipentaerythritol esters of oleic, linoleic and linolenic acids in a similar manner. They also found that the band at about 2.8 microns increases and the band at 3.27 microns decreases during the drying process and interpreted this observation as support for the theory that during the initial stages of autooxidation of drying oils, the first step is the formation of hydroperoxides on the carbon atom alpha to the double bonds. Nicholls and Hoffman also showed that the infrared spectra of pentaerythritol esters of linseed oil fatty acids, blown linseed oil, heat polymerized linseed oil and other substances exhibit an —OH stretching band at about 2.9 microns which progressively increases, indicating formation of hydroxyl, —OH, or hydroperoxide, O—O—H, groups.

O'Connor has summarized in some detail applications of infrared absorption spectra to autooxidation and drying oil mechanism in his review;¹ Crecellius, Kagarise and Alexander¹³ credit infrared spectroscopy (along with ultraviolet) with considerably stepping up progress toward understanding drying oil oxidation mechanisms. They discuss in detail interpretation of the changes in infrared spectra during drying in their excellent review entitled "Studies of the Mechanisms of Drying Oil Oxidation."

Quantitative Applications in the 3 Micron Region. Using plots of the ratio of the absorptivities at 3.20 microns (—OH stretching) to that at 3.43 microns (C—H stretching), Bayzer, Schauenstein and Winsauer¹⁴ determined the hydroxyl content of hydroxy acids. The ratio 0.443 for 12-hydroxystearic acid is directly proportional to the number of —OH groups in di-, tetra- and hexa-hydroxystearic acids. Kabasakalian,

Townley and Yudis¹⁵ found that the number of —OH groups contained in a steroid molecule can be determined by use of the fundamental —OH stretching absorption. Absorbance of the associated 3.05 micron —OH band was shown to be linear with concentration and independent of the type of hydroxyl group.

Thomas¹⁶ used infrared absorption in the 3 micron region to determine the concentration of the alcoholic —OH and the carboxyl COOH groups quantitatively, in the same molecule, as in omega-hydroxypalmitic acid. In very dilute solution the —OH stretching vibration occurs at 2.74 microns, the position of free —OH. The —OH stretching of the COOH group, however, even in very dilute solution, is bonded, probably as a single bridge dimer, and the band appears at 2.84 microns. Davies¹⁷ has shown that, even in very dilute solution, —OH bonding still exists (20 %) in omega-hydroxyundecanoic acid by reason of intracyclization,



The 5-6 Micron Region

The wavelength interval between about 5.0 and 6.5 microns is the region of double bond stretching vibrations (see Table 1). Of particular interest to the lipide chemist are the C=O stretchings of acids, esters, ketones, aldehydes, anhydrides, and lactones, all of which exhibit characteristic bands in this region. The C=C stretching vibration is also seen in this region at about 6.1 microns. McCutcheon, Crawford, and Welsh¹⁸ used this band to distinguish between *cis* and *trans* unsaturation. They measured the spectra from 5 to 6.5 microns and used the very weak band at 6.0 microns assigned to a C=C stretching. Theoretical considerations show that the *cis* double bond should absorb at 6.0 microns while the *trans* bond should

not. Using ethyl stearate as a blank to cancel the very strong C=O absorption in this region, it could be shown that oleic acid had a *cis* configuration, linoleate a *cis, cis*, and linolenate a *cis, cis, cis* structure. Elaidic acid similarly was shown to be the *trans* isomer and linelaidate to have a *trans, trans* configuration. Raman spectra have confirmed these results. However, because the C=C stretching vibration band at 6.0 microns is very weak, and since there is interfering absorption from the strong C=O stretching vibration, this method has not proved very satisfactory. More accurate identification and determination of unsaturated double bonds can be made using the near infrared for *cis* and the 10 micron region for *trans* double bonds.

Morris,¹⁹ in a review of investigations on the mechanisms of fat oxidation and its relation to rancidity, includes a discussion of the role of infrared spectroscopy, emphasizing the important gains in the understanding of these complex reactions by means of this tool. The C=O stretching vibrations of various fatty acid derivatives between 5 and 6.5 microns (see Table 1) have enabled several workers to follow the course of autooxidation, rancidity and the development of off-flavors.

A. S. Henick²⁰ has investigated the auto-oxidation of milk fat by observation of changes in the infrared spectra of the volatile components. An off-flavor, off-odor sample of milk was steam-distilled *in vacuo*, and the infrared spectra of the distilled fraction examined in CS₂ solution. In the range of C=O stretching, bands appear at 5.77, 5.81, 5.91, and 6.11 microns. For comparison, the spectra of fresh milk were examined and shown to exhibit only two bands in this region, at 5.80 and 5.75 microns. Upon storage the 5.80 micron band remains unchanged but the 5.75 micron band shifts to 5.70 microns. With longer storage new peaks appear at 5.86 and 5.91 microns and still longer storage results in the appearance of a band with

maximum at 6.10 microns, which increases in intensity as the storage period is increased. The bands at 5.91 and 6.11 microns were shown to arise from conjugated ketones, aldehydes being eliminated by negative Schiff tests. Infrared spectrophotometry was found to be more sensitive to changes than a qualified taste panel and considerably more sensitive than peroxide value determinations. Chang and Kummerow²¹ used infrared spectra to detect the ketonic carbonyl group at 5.83 microns in the presence of the ester carbonyl group at 5.75 microns, thereby settling a controversial point by proving that oxidation polymers of ethyl linoleate are linked through carbon to oxygen bonds rather than carbon to carbon bonds. Molaison, O'Connor and Spadaro²² used the disappearance of the 5.78, C=O, band to confirm completion of reaction in their preparation of long-chain unsaturated alcohols from jojoba oil by sodium reduction.

Quantitative methods were suggested by Harrison and Tolberg²³ in connection with their investigations of the effects of several fatty acids on the polymerization of styrene. They established a multicomponent system of analysis with methyl and ethyl benzoate, measured at 5.70 microns, as the standard for benzoate; methyl stearate, measured at 5.75 microns, for the fatty esters; and heat polymerized, carboxyl-free polystyrene, for the polystyrene. Measurements were made at only the two carboxy frequencies since the contribution of polystyrene was small and constant.

The amount of ester wax present in emulsion polish was estimated by Murphy and Schwemer²⁴ from a comparison of the intensity of the 5.75 micron band with that of the CH₂ and CH₃ deformation band at 6.81 microns. The benzene ring deformation band at 6.61 microns was used in a similar fashion to determine the per cent of phenolic resin in the emulsion formulation. Bands at 5.78 microns, characteristic of the ester, and at 6.10 microns, characteristic of the morpho-

lide, were used by Dupuy, O'Connor and Goldblatt²⁵ for diagnostic purposes and for analysis of morpholides of ricinoleic acid and some of its derivatives.

An investigation of the spectra of iodolactonization of acids lead van Tamelen and Shamma²⁶ to suggest a method, based on measurement of bands in the 5 micron region, for the determination of the position of double bonds. A band at 5.6 microns in the spectrum of the iodolactone indicates that the starting acid was probably *beta-gamma* or *gamma-delta* unsaturated. Absorption at 5.75 microns demonstrates the probable presence of a *delta-epsilon* double bond.

In the spectra of natural fats and oils the

appearance of additional bands about the 5.72 micron band of the ester C=O stretching indicates the formation of aldehydes, ketones or acids. These measurements are frequently difficult because of insufficient resolution in this region. Dugan, Beadle and Henick report that absorption arising from keto and aldehyde carbonyl appears only as indefinite shoulders on the strong bands due to ester carbonyl. In spite of these limitations, however, infrared spectroscopy has made a considerable contribution to the understanding of autooxidation, rancidity and drying oil mechanism. Increasing availability of instruments providing considerably higher resolution will unquestionably afford more and better information from investigations in these fields.

The 10 Micron Region

Determination of Isolated Trans Bonds. In 1947 Rasmussen, Brattain and Zucco²⁷ showed that a strong band at 10.3 microns appears in the infrared spectra of all unsaturated compounds which contain a *trans* C=C group. This band was subsequently shown to arise from a C—H deformation about a *trans* C=C in the internally unsaturated group RHC=CHR.²⁸ The band is illustrated in Figure 2. This is the type of unsaturation most frequently encountered in fatty acid chemistry, and this band has been used to develop quantitative methods for the determination of isolated *trans* isomer unsaturation. Shreve and co-workers²⁹ describe a specific procedure using this band for the quantitative determination of internal, isolated *trans*-bond concentration in mixtures of saturated and monounsaturated octadecenoic acids and related compounds. For the isolated *trans* bond they reported an absorptivity in CS₂ solution of 0.4. Paschke, Jackson and Wheeler³⁰ showed that this absorptivity is about the same in the absorption spectra of pure methyl *cis*-9, *trans*-12-linoleate and that the absorptivity of the band in the spectra of pure methyl linelaidate

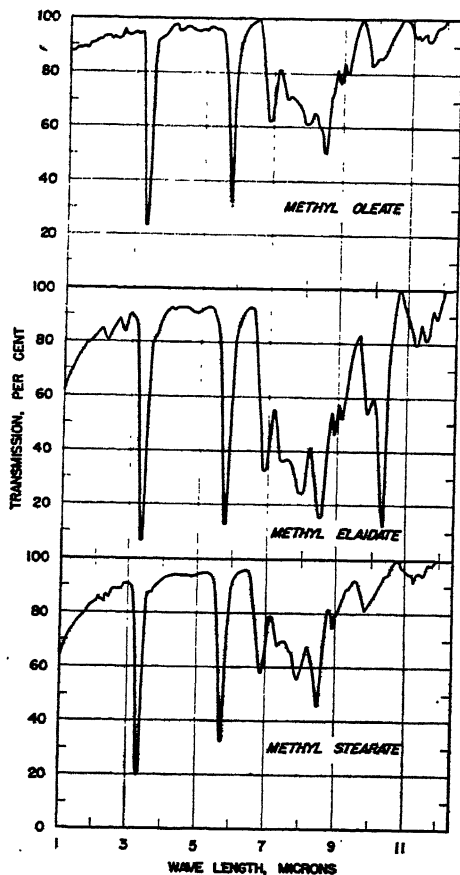


FIG. 2. Infrared absorption spectra of *cis* and *trans* isomers. Methyl oleate, methyl elaidate and methyl stearate in CHCl₃ solution.

(*trans*-9, *trans*-12) was very nearly twice this value. Bickford and his co-workers³¹ found that the absorptivity at 10.1 microns in the spectra of *alpha*-eleostearic acid (*cis*-9, *trans*-11, *trans*-13-octadecatrienoic) is exactly twice that reported for elaidic acid and that in the spectra of *beta*-eleostearic acid (*trans*-9, *trans*-11, *trans*-13-octadecatrienoic) it is three times that of elaidic acid. These data are interpreted to indicate that intensities of the C—H deformation about the C=C group are additive in both non-conjugated and conjugated compounds. The position of absorption is identical for all isolated (i.e., non-conjugated) *trans*-octadecenoic acids, esters and their glycerides. The procedure can be used for the determination of isolated *trans* isomer content in nonconjugated polyunsaturated as well as in monounsaturated compounds. The method has been compared with the lead salt-alcohol method for determining *trans*-octadecenoic acid by Swern, Knight, Shreve and Heether³² and by Jackson and Callen.³³ Both groups reported that the infrared method was more rapid, more specific, and more accurate. The Spectroscopy Committee of the American Oil Chemists' Society has, after a long collaborative study, recently recommended a procedure for adoption as an official method of the Society.³⁴

Trans Bonds in Conjugated Systems.

C—H bending about the double bond in conjugated compounds has been investigated by Jackson *et al.*³⁵ and by Ahlers and co-workers.³⁶ Jackson *et al.* were the first to show that a single very strong band is exhibited at 10.12 microns in *trans*, *trans*-linoleate. This assignment confirmed a very much earlier suggestion of Gamble and Barnett.³⁷ Conjugated *cis*, *trans*-linoleate was shown to exhibit two maxima, a strong band at 10.18 microns and a somewhat weaker band at 10.52 microns. Only a very weak band with maximum at 10.95 microns was found in the spectra of conjugated *cis*, *cis*-linoleate. Ahlers *et al.* published results of a detailed quantitative study of some 19 fatty acids, including

monounsaturated and conjugated and non-conjugated polyunsaturated compounds. They confirmed earlier published results for wavelength positions of the bands and reported reasonably good agreement with previously reported absorptivities for the few cases where these values had been measured earlier. These workers account for the position of maxima in the spectra of conjugated acids containing *trans* bonds as a hypsochromic shift from the position of the isolated *trans* band, small but significant and consistent with the effect of conjugation on the C—H deformation frequency of the system. The exact positions of maxima absorption are given in Table 2. O'Connor,³⁸ in a paper presented before the American Oil Chemists' Short Course in 1958, extended this postulation to the isolated *cis* system (Table 2). This addition accounts for the appearance of two bands in the spectra of *cis-trans* conjugated acids. However, the *cis* bands in this region have been shown to be very weak and quite variable in position with changes in molecular environment. They are not satisfactory for diagnostic purposes. Determination of *cis* unsaturation by means of infrared spectra appears to be limited to measurements in the near-infrared region where satisfactory results are being reported.

Chipault and Hawkins³⁹ used the bands given in Table 2 to devise a specific procedure for the determination of conjugated *cis-trans* and *trans-trans* octadecadienoates. *Cis-trans* compounds alone or in the presence of *trans-trans* isomers can be determined directly from measurements of the absorptivity at 10.55 microns. *Trans-trans* compounds, in the absence of *cis-trans* may be determined directly from the absorptivity at 10.11 microns. In the presence of *cis-trans* isomers, *trans-trans* conjugation can be obtained by a measurement of *cis-trans* plus *trans-trans* compounds, from absorptivities at 10.11 microns, and subsequent correction of this measurement for *cis-trans* content obtained

INFRARED SPECTROPHOTOMETRY

TABLE 2. C—H DEFORMATIONS ABOUT THE C=C, ETHYLENIC, GROUP IN THE 10-15 μ REGION

No.	Wavelength position of observed absorption band	Vibrating group giving rise to observed absorption band
	microns	
1.	10.05-10.15	$\begin{array}{c} \text{X} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$
2.	10.20-10.36	$\begin{array}{c} \text{X} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & , (trans) \\ & / & \diagdown \\ \text{H} & & \text{Y} \end{array}$
2a.	10.34	Isolated <i>trans</i>
2b.	10.17	<i>Cis</i> , <i>trans</i> -conjugated
2c.	10.12	<i>Trans</i> , <i>trans</i> -conjugated
2d.	10.11	<i>Cis</i> , <i>cis</i> , <i>trans</i> -conjugated
2e.	10.09	<i>Cis</i> , <i>trans</i> , <i>trans</i> -conjugated
2f.	10.06	<i>Trans</i> , <i>trans</i> , <i>trans</i> -conjugated
3.	10.90-11.05	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{X} & & \text{H} \end{array}$
4.	11.17-11.30	$\begin{array}{c} \text{X} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{Y} & & \text{H} \end{array}$
5.	11.90-12.50	$\begin{array}{c} \text{X} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{Y} & & \text{Z} \end{array}$
6.	13.0 > 15.0	$\begin{array}{c} \text{X} & & \text{Y} \\ & \diagdown & / \\ & \text{C}=\text{C} & , (cis) \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$
6a.	10.95	Isolated <i>cis</i>
6b.	?	<i>Cis</i> , <i>cis</i> -conjugated
6c.	10.53	<i>Cis</i> , <i>trans</i> -conjugated

from measurement at 10.55 microns. The method has been used to follow conjugated *cis-trans* and *trans-trans* isomerizations accompanying alkali isomerization of linoleic acid under the influence of several catalysts and under different conditions.

Determination of Terminal Double Bonds. Measurements of infrared absorption bands in the 10 micron region have not been limited to identification and determination of internal double bonds. An early use of infrared spectroscopy in this region was to determine whether the C=C group was internal or a terminal group, and if terminal whether an isopropenyl, isopropylidene, etc. Bands which are used for these purposes are included in Table 2.

Trans Isomer Measurements and the Structure of Constituents in Natural Commodities. Applications of the infrared absorption methods to identify and determine isolated *trans* isomers have been increasing continually and now scores of examples of the use of this technique have been reported in the technical literature.^{1, 2, 40}

The method for the determination of isolated *trans* isomers by means of infrared spectroscopy has been applied by several workers either for the elucidation of structure or to ascertain the presence (or absence) of specific constituents in natural commodities. Thus, Swern, Knight and Eddy found that a sample of freshly rendered edible beef fat, and of edible oleo oil and oleo stearin obtained from it, contained substantial quantities (5 to 10%) of *trans* material believed to be mainly, if not exclusively, monounsaturated. *Trans*-6-octadecenoic (elaidic) and *trans*-11-octadecenoic (vaccenic) acids were isolated from oleo oil, the former apparently for the first time. Vaccenic acid was also prepared from beef tallow by Rao and Daubert. By comparing its infrared spectra with that of oleic and elaidic acids they showed that vaccenic acid is the *trans*-11-octadecenoic acid. Ahmed, Bumpus and Strong synthesized *cis*-11 and *trans*-11 octadecenoic acids and showed, by infrared curves, that the *trans* acid was *trans* and identical with Rao and Daubert's vaccenic acid from beef tallow. Khan, Deatherage and Brown, and Max and Deatherage demonstrated by means of infrared spectra the complete ab-

sence of *trans* bonds in synthetic methyl 9,10-dideuterooleate and 8,8,11,11-tetra-deutero,*cis*-9-octadecene, respectively.

Paschke, Tolberg and Wheeler used the infrared method in a study of the *cis-trans* configuration of *alpha* and *beta* eleostearic acids. Both isomers reveal a strong band at about 10.1 microns, indicating a *trans*, *trans*-conjugated configuration, in agreement with the fact that they both form maleic anhydride adducts readily below 100°C. The spectra of the *alpha*-eleostearic acid adduct exhibited no band at 10.3 microns, indicating that the third unsaturated C=C, not affected by the maleic anhydride addition, is a *cis* bond. The spectra of the maleic anhydride adduct of *beta*-eleostearic acid, however, did exhibit a band at 10.36 microns, indicating that the third unsaturated bond in this molecule is *trans*. Thus *alpha*-eleostearic acid has two *trans* and one *cis* bond and *beta*-eleostearic acid is the *trans,trans,trans* isomer.

Pseudo-eleostearic acid was shown to have the same structure as *beta*-eleostearic acid and *alpha*- and *beta*-licanic acids (4-keto-9,11,13-octadecatrienoic acids) the same *cis-trans* configuration as *alpha*- and *beta*-eleostearic acids. Punicic acid is a *cis, trans*-isomer of *alpha*- and *beta*-eleostearic acid, not identical with either. Ahlers *et al.* subsequently showed, also by infrared spectra, that it has a *cis, cis, trans*-configuration. Bickford, DuPre', Mack and O'Connor confirmed the results of Paschke *et al.* on the structure of the eleostearic acids. A band in the spectra of the maleic anhydride addition product with butadiene at 10.40 microns was assigned as one of the symmetrical "breathing" vibrations of a substituted maleic anhydride ring. As a similar band might interfere with the 10.36 micron band, to be used as evidence for the presence or absence of an isolated *trans* bond in the spectra of the *alpha*- and *beta*-eleostearic acid maleic anhydride addition products, the adducts were converted to the corresponding tri-*n*-butyl

esters. The spectra of these esters, which do not have maleic anhydride rings, would not be expected to exhibit the band at 10.40 microns. The infrared spectra of the tri-*n*-butyl ester of the *beta*-eleostearic acid exhibited a pronounced band at 10.36 microns, while no trace of a corresponding band was found in the spectra of the ester of the *alpha*-eleostearic acid adduct. Thus additional evidence was obtained to establish the fact that *alpha*-eleostearic acid has one *cis* and two *trans* bonds and that there are three *trans* bonds in *beta*-eleostearic acid.

Trans Bonds and Hydrogenation. The infrared method for isolated *trans* isomers has been found useful in investigations of the hydrogenation of vegetable oils and animal fats. Jackson and Callen³³ showed that hydrogenated oils contain *trans* or "iso"oleic acid. Lemon and Cross showed that hydrogenation is accompanied by a *cis* to *trans* change in some of the double bonds of the unsaturated fatty acid by the appearance of the 10.3 micron band in the spectra of the hydrogenated products. Workers in Daubert's Laboratory⁴¹ followed the hydrogenation of methyl *beta*-eleostearate. The principal changes were the disappearance of the band at 10 microns (*trans,trans*-conjugation) and the appearance of a band at 10.3 microns (isolated *trans*). A partial hydrogenation of methyl linolenate yields a mixture of at least three isomers, the 8,14- 9,15- and 10,14-isolinoleic acids. Infrared spectra were used also to show that the 8- and 9-octadecenoic acids produced during hydrogenation of triolein are the *trans*-isomers.

Lemon showed graphically the formation and disappearance of *trans* double bonds during the hydrogenation of vegetable oils. Sims and Hilfman repeated some of this work and extended it to animal fats. They found that conditions which favor the development of *trans*-isomers also favor selective hydrogenation of the glyceride oils and that unusually high percentages of

trans-isomers develop during hydrogenation of tallow.

Feuge and co-workers⁴² have reported on the quantitative investigation of the hydrogenation of methyl oleate and triolein and the hydrogenation of methyl linoleate and cottonseed oil. In connection with their investigations of the positional isomers formed, workers in this laboratory have used the infrared method to detect and determine *trans* bonds formed during the hydrogenation of cottonseed oil and methyl linoleate, respectively.

In their analysis of the monoethenoic fatty acids of butterfat, Backderf and Brown⁴³ used the infrared absorption method for the determination of *trans*-isomers. By this means they established: (a) the presence of a previously unreported acid, *trans*-10-octadecenoic, present to the extent of 1–2% of the total butterfat fatty acids; (b) that over 20% of the hexadecenoic acids of butterfat had the *trans* configuration, accounting for about 0.4% *trans* acids of the total butterfat fatty acids, previously unreported; and (c) that 11-octadecenoic acids, found to be present to the extent of 3–4% of the total butterfat fatty acids, were mostly *trans*, with inconclusive evidence of the presence of the *cis* isomer. Scott, and co-workers⁴⁴ have also investigated the fatty acid composition of butterfat, and confirm the presence of C₁₀ to C₁₈ monoethenoic acids. The *cis* form was predominate in the C₁₂ and C₁₄ acids, while the C₁₆ and C₁₈ compounds occur as both *cis* and *trans* isomers. Nonconjugated dienoic acids consisted of mixtures of either *cis-cis* and *cis-trans* or *cis-cis* and *trans-trans* and conjugated dienoic acids were either *cis-trans* or *trans-trans*. Trienoic, tetraenoic and pentaenoic acids all occur only in the *cis* configuration.

Trans-Isomers and Autooxidation. A third major application of the infrared absorption of the *trans* bond in the 10 micron region has been in investigations of autooxidation.¹ These infrared absorption studies

have definitely established that the initial product of the autooxidation of monounsaturated *cis*-compounds is the isomeric *trans*-hydroperoxide, and that diunsaturated *cis*-compounds result in the formation of conjugated *cis, trans*-hydroperoxides at 0°C and conjugated *trans, trans*-hydroperoxides above room temperature.

The formation of *trans* double bonds during the autooxidation of monounsaturated methyl oleate by ultraviolet radiation was demonstrated by Knight, Eddy and Swern. Increase in the absorption at 10.3 microns relative to the peroxide value was interpreted as indicating that most of the peroxides formed are *trans*-peroxides. Swern *et al.* extended these investigations showing, by means of infrared absorption measurements, that in the autooxidation of methyl oleate between 35 and 120°C most, if not all, of the hydroperoxide formed has the *trans*-configuration, regardless of whether the autooxidation is conducted in the dark or in the presence of ultraviolet radiation. The autooxidation of methyl linoleate was investigated by means of infrared absorption by Khan and Privett and by Cannon *et al.* These investigations showed that on autooxidation of methyl linoleate at 0°C at least 90% of the initially formed hydroperoxide has a *cis, trans*-conjugated arrangement of double bonds. At room temperature less *cis, trans*- and some *trans, trans*-conjugation was found, indicating to Khan and Privett that at higher temperatures a further isomerization to *trans, trans*-form occurs. Cannon *et al.* confirmed these conclusions showing that autooxidation of methyl linoleate at 0°C leads to the formation of about 90% *cis, trans*-hydroperoxide, while at room temperature the *trans, trans*-hydroperoxide predominates. Privett and co-workers showed that both methyl linoleate and methyl linolenate formed a *cis, trans*-conjugated monomeric monohydroperoxide as the major initial product of autooxidation at 0°C. Using ultraviolet absorption along with infra-

red, they concluded that at least 90 % of the conjugated hydroperoxides formed from normal methyl linoleate at 0°C were *cis*, *trans*-conjugated and that at higher temperatures a considerable amount goes to the *trans*-form exclusively.

Harrison and Wheeler, again by means of infrared absorption, found that the products obtained in the autooxidation of methyl linoleate and methyl linelaidate with di-*t*-butyl peroxide were mixtures of isomers. Selected fractions from distillation all showed about 90 % of the theoretical value for two double bonds per linoleate unit or four per dimer, but some fractions were rich in *cis*, *trans*-conjugated configuration, others were mostly *trans*, *trans*-conjugated, while still others had relatively large amounts of isolated *trans* double bonds.

The *trans* fatty acid content of several animal and vegetable fats was investigated by Kuhn and Luck.⁴⁵ They questioned the hypothesis that only ruminant animals deposited fat containing *trans* fatty acids as 3.5 % was found in human fat and 4.0 to 6.3 % in the fat of the domestic cat. Irradiation of lard and olive oil in air increased the intensity of the infrared *trans* band until a limiting value of about 6–8 % was reached. Ultraviolet irradiation of beef fat caused an increase (from 5 to 8 %) of *trans*-fatty acids, but irradiation of hydrogenated peanut oil containing about 30 % *trans*-olefins caused a slow decrease in *trans*-isomer content.

McCutchon and co-workers⁴⁶ showed that both the wavelength position and the intensity of the C—H deformation about the C=C were effected, presumably by some influence of the O—H group, in the spectra of ricinelaidic acid (*trans*-12-hydroxy-9-octadecenoic acid) and its methyl ester. The characteristic band in the 10 micron region exhibits a hypsochromic shift, from 10.33 microns in CS₂ solution, for methyl elaidate, to 10.27 microns for the methyl ricinelaidate. The absorptivity is also somewhat less for the ricinelaidate. They proposed equations

for the determination of both the acid and its methyl ester. These same workers studied the absorptivities and the positions of maxima in the 10.3 micron region of the infrared spectra of several derivatives of ricinelaidic acid. Observed decreases in molecular absorptivities and shifts in position of maximum absorption as the functional groups of ricinelaidic acid when varied systematically were related to the electron-withdrawing character of the relevant substituent and to the hydrogen bonding in the *beta*-hydroxyene system.

Oxidation of methyl ricinoleate with *tert*-butyl chromate was shown to result in a partial isomerization of the *cis*-methyl ricinoleate to *trans*-methyl ricinoleate (methyl ricinelaidate) by Maruta and Suzuki.⁴⁷ *Cis*-to *trans*-interconversions of methyl oleate, linoleate and linolenate when treated with oxides of nitrogen were investigated by Khan⁴⁸ by means of infrared determinations. *Trans*-isomers from methyl linoleate and linolenate were less than 5 %, from methyl oleate, 35 %.

Absorption in other Regions of the Infrared Spectrum

Measurements in the near-infrared region (from 0.8 to 2.5 microns), in the region of fundamental O—H stretching vibrations (about 3.0 microns), in the region of double bond stretching vibrations (from 5 to 6 microns), and in the region of C—H deformations about double bonds (near 10 microns) have been of greatest value to the lipide chemist. Absorption in almost every other region of the spectrum has found special uses. In studies of molecular structure and of the identification of individual components, bands in the triple bond region, about 4 microns, in the region of single bonded C—O stretching, 8 to 10 microns, and in the region of deformation about ring structures, above 11 microns, have proved to be of interest in specific applications.

Applications to Tissue Lipides, Serum

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Lipides, Lipoproteins and Phospholipides. The infrared spectra of synthetic *alpha*-cephalins of the L-series, which constitute a homologous series of pure phospholipides, were investigated by Baer and co-workers.⁴⁹ The spectra of distearoyl di-

TABLE 3. INFRARED BANDS USED IN ANALYSES OF PHOSPHOLIPIDES

Wave-length (microns)	Constituent	Vibrational Group
2.8	Protein, Phospholipide	N—H, O—H stretching
3.0		
4.6	Ethanolamine	Unassigned
4.7	Containing Phospholipides	
5.75	Glycerides	C=O ester stretching
5.85	Free Fatty Acids	C=O acid stretching
6.0	Cholesterol	C=C stretching
6.1	Protein (sphingomyelin)	C=O amide stretching
6.5	Protein (sphingomyelin)	C=O stretching and N—H bending
6.7	Phospholipides	CH ₂ , CH ₃ bending
7.5	Phospholipides	CH ₂ , CH ₃ bending
7.8	Free Fatty Acids	COOH
8.1	Phospholipides	P=O stretching
8.2	Phospholipides	C—O—C stretching
8.55	Cholesteryl Esters	C—O stretching
8.65	Fats (Lecithin)	C—O stretching
9.2	Phospholipides	P—O—C stretching
9.9	Ethanolamine Containing Phospholipides	C—O—C ?
10.3	Phospholipides	P—O—C stretching
10.3	Lipides	$\begin{array}{c} \text{H} \\ \text{Trans C}=\text{C} \\ \text{H} \end{array}$
10.65	Free Fatty Acids	O—H of COOH
11.9	Cholesteryl Esters	C—H bending adjacent to C=C
12.1	Cholesteryl Esters	C—H bending adjacent to C=C
14.3	Free Fatty Acids	—H —H
14.4	Phospholipides	Cis C=C
14.7	Lecithin	$\begin{array}{c} \text{H H} \\ \text{Cis C}=\text{C} \end{array}$

palmitoyl- and dimyristoylcephalin were measured and several band correlations reported. The spectra are not identical, as in the case of the corresponding straight chain fatty acids, but several rather large and unexplained differences were found in the region above 11.0 microns.

Freeman and co-workers at the Donner Laboratory of Biophysics and Medical Physics, University of California,⁵⁰ and Schwarz at the Biochemistry Department of the Philadelphia General Hospital⁵¹ have reported several investigations of the infrared spectra of serum lipides and of tissue lipides, respectively.

Freeman and co-workers have studied infrared spectra of solutions of serum lipides, lipoproteins and related lipides in thin cells. They have compared the spectra of lipoproteins isolated from human blood serum with the spectra of reference compounds. Making several correlations by direct comparisons, they have suggested that infrared bands can be used to identify components and to determine them quantitatively by means of multicomponent analyses. The spectra of serums are weak, however, with respect to individual components, and a more satisfactory technique was found to be a column chromatographic separation into specific fractions each of which was then analyzed in turn by means of infrared absorption spectra. Using this combination of chromatography on activated silicic acid-Celite (2:1) and infrared spectrophotometry in carbon disulfide and chloroform solutions, these workers have described multicomponent methods of analysis for cholesteryl esters, glycerides, unesterified cholesterol, unesterified fatty acids, phosphatides, protein, lecithin, etc., using the bands tabulated in Table 3.

Schwarz and co-workers have similarly resorted to a combination of column chromatography and infrared absorption spectroscopy to determine components in tissue lipides. This group has adopted the KBr disc technique for the measurement of frac-

tions from silicic acid powder columns, and described these techniques for the determination of sphingomyelin, cephalins, lecithins, free cholesterol, etc., by means of the band correlations given in Table 3.

Marinetti and Stotz,⁵² studying the infrared spectra of phospholipides, sphingomyelin and related lipides in connection with investigations of structural configuration, showed that the P—O—C linkage gives rise to a band at 10.3 microns, but that this band can be differentiated from that arising from C—H deformation about the *trans* C=C as the latter completely disappears on hydrogenation while the P—O—C linkage is unchanged. These workers also presented the spectra of several lipides and a complete analysis of the bands and groups giving rise to them.

In other investigations of lipide chemistry, Renkonen and Koulumies⁵³ compared the spectra of serum lipides from normal individuals and from young and old diabetics with the spectra of pure lipides. Hanahan and Jayko⁵⁴ compared the spectra of dipalmitoleyl-*L*- α -glycerylphosphorylcholine with its hydrogenation product dipalmitoyl-*L*- α -lecithin and with that of palmitoleic acid.

A combination of paper chromatography and infrared spectrophotometry was used by Labarrere and co-workers⁵⁵ to establish an analytical procedure for separation and identification of cholesteryl esters. The method was tested by the paper chromatographic separation and infrared identification of synthetic mixtures of cholesteryl laurate, myristate, palmitate, stearate, oleate, linoleate and linolenate. Separations were made by ascending reversed-phase paper chromatography using two solvent systems, acetone-ethanol-formic acid-water and chloroform-methanol-formic acid-water, consecutively on the same paper strip. Identifications of the fractions were made by means of infrared absorption spectra. The entire procedure requires only a few milligrams of pure sample.

The infrared bands used for the identifications included in Table 3 are discussed in detail.

Elucidation of Molecular Structure of Fatty Acid Materials. In a series of four papers, Celmer and Solomon described the proof of the structure of mycomycin and isomycomycin mainly through the use of infrared absorption spectra. The essential steps in their proof have been outlined by Wheeler.⁴⁰ The presence of a cyclopropane ring in lactobacillic acid, as demonstrated by means of infrared absorption spectroscopy by Hofmann, Lucas and Sax and in sterculic acid by Nunn, are also reviewed by Wheeler.

Freeman and co-workers resorted to infrared spectra to prove the structure of the C₂₇ phthenoic acids isolated from crude methyl phthenoate. A summary of this work and references to the original papers will be found in the review by O'Connor.¹ The work of Davis and co-workers in the identification of the hypotensive principle of tung oil as 9,14-dihydroxy 10,12-octadecadienoic acid, and of Walborsky *et al.* of the use of infrared spectra to confirm the absence of allene structure conjugated with an acetylenic group and the absence of *trans*-isomers in the total synthesis of linoleic acid, are cited as further examples of the use of infrared absorption spectra for purposes of identification of molecular structures.

Miscellaneous Applications in Diverse Regions of the Infrared Spectrum. During the past few years not only have the number of applications of infrared spectroscopy to problems of the fatty acid chemist increased but the diversity of types of applications has been spreading, as evidenced by the review of the literature by Kaufmann.² Lecomte⁵⁶ has reviewed applications of infrared spectroscopy to fats; Favier⁵⁷ Hires and Balog⁵⁸ and Minutilli⁵⁹ to vegetable oils; and D'Arrigo⁶⁰ to fish oils. The important problems of the detection of adulteration of olive oil has been attacked by infrared spectroscopy by Minutilli⁶¹ and by Bottini and

Sapetti.⁶² Bartlet and Mahon⁶³ have published a method for the identification of oils and of oil adulteration by differential infrared spectroscopy.

Infrared spectra have been applied to a survey of rare plants in a search for new industrial oils by Earle and co-workers⁶⁴ and was used by Glass and Melvin⁶⁵ in the determination of the composition of vinyl copolymers.

Dupuy and co-workers⁶⁶ showed that the intensity of the characteristic nitrile group at 4.44 microns in the spectra of five ricinoleic acid derivatives cyanoethylated with acrylonitrile is about 67% greater in chloroform than in carbon tetrachloride and that, as it obeys Beer's law over a wide range of concentrations, infrared spectra permit a convenient analysis for this type of compound. Fore⁶⁷ *et al.* used infrared spectra to characterize the reaction products of mercaptoacetic acid with methyl linoleate and linoleic acid; Pratt and Wender⁶⁸ to identify rutin and isoquercitin in cottonseed; Brunn⁶⁹ in an investigation of the structure of the newly discovered palustic acid; and Fuchs

and Dieberg⁷⁰ in a solution of the montanic acid problem.

Solid State or Crystalline Spectra

Jones, McKay and Sinclair,⁷¹ in their survey of the infrared spectra of long-chain fatty acids and related compounds, observed that significant differences exist when the spectra of these materials in solution are compared to the spectra in the solid state. The 13.9 micron methylene rocking vibration is split into two bands in the solid state spectra, but the principal difference is observed in the region between 7.5 and 8.5 microns. In the spectra of saturated fatty acids in solution a broad intense band is observed throughout this region. In the crystalline state, this broad band is resolved into a series, or progression, of bands, very evenly spaced, the number of individual bands depending upon chain length. The spectra of several saturated fatty acids in this region are reproduced in Figure 3 to illustrate how this region, in crystalline spectra, can be used to determine chain length. A band in the progression is observed for each pair of

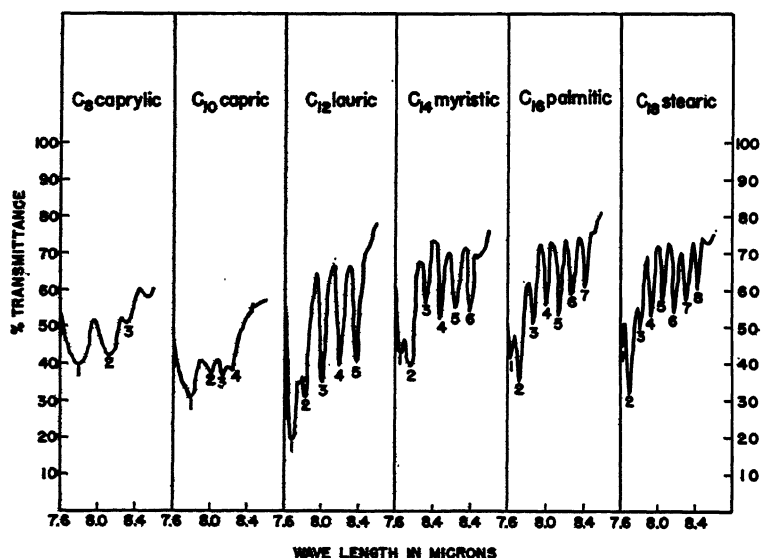


FIG. 3. Crystalline state infrared spectra in KBr discs-determination of chain length in saturated long-chain fatty acids. Caprylic, capric, lauric, myristic, palmitic and stearic acids.

methylene groups. Thus by counting the number of observed bands and doubling it and adding two (one for the carboxyl group and another for the terminal methyl group) the length of the chain can be determined.

Meiklejohn and co-workers⁷² investigated the infrared spectra of a very large number of fatty acids, esters and related compounds and showed that this progression of bands could be used as a reliable indication of chain length. Susi⁷³ later investigated the solid state spectra of unsaturated fatty acids and showed that the C=C group acts as a terminator, the number of bands in the 7.5 to 8.5 micron progression depending upon the number of methylene groups between the carboxyl and the double bond. Thus, in monounsaturated compounds, the number of observed bands is an indication of the position of the double bond.

Jones *et al.*⁴⁶ had observed differences in the infrared spectra of various polymorphic forms of the fatty acids, differences which they believed would make solid state spectra less useful than solution spectra for diagnostic purposes. Cornish and Chapman⁷⁴ investigated the infrared spectra of crystalline long-chain compounds, including monocarboxylic acids, and showed how by means of infrared absorption spectra polymorphic forms could be differentiated. They were able to establish a correlation between the CH₂ rocking vibrations and the type of packing between the chains. Excellent correlation was established for the orthorhombic and triclinic sub-cells (the two major types), and infrared spectra in the crystalline state.

In a series of six papers Chapman⁷⁵ showed that the infrared spectra of glycerides could be used to establish their polymorphic form. These investigations confirmed the existence of the Alpha, Sub-Alpha, Beta and Beta-Prime forms of these materials, in agreement with the views of Lutton, from x-ray examination and contrary to the views of Malkin. Infrared solid state spectra seem to have finally settled this long controversy as to the

interpretation of x-ray diffraction data. Chapman and co-workers published an application for this type of data⁷⁶ showing, from solid state infrared absorption data, that the major disaturated glyceride of cocoa butter is 2-oleopalmitostearin and not 2-palmitooleostearin as commonly believed, but that this latter compound, 2-palmitooleostearin, is the major disaturated glyceride of lard. Thus it appears that solid state infrared absorption spectra may: (a) provide a measure of chain length; (b) afford a clue as to position of a double bond; and (c) differentiate among polymorphic forms.

"Fingerprint" Identification

All of the applications of infrared absorption spectroscopy described in this article have been applications of the "group frequency" methods of analysis. As mentioned earlier, the fatty acid chemist has not had at his disposal a sufficient library of infrared absorption spectra of pure compounds for use of the "fingerprint" detection techniques, i.e., identification by direct comparison of the spectra of an unknown with a series of spectra of known molecules.

Applications of the "fingerprint" technique involve two paradoxical problems. At first the specific laboratory does not have sufficient spectra of pure compounds in which it is interested to permit "fingerprint" identification. Hence it has been necessary for each individual laboratory to prepare, from suitably pure compounds, spectra for its own needs. As this library of spectra grows and before it is of a size sufficient to permit identifications by direct fingerprint comparisons, it has become so large that matching in this manner has become a time-consuming problem.

These two problems were investigated by the American Society for Testing Materials. Committee E-13 on Absorption Spectroscopy proposed a dual solution. First it would undertake to collect spectral data from all available sources and make them available

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to all infrared absorption laboratories, thus avoiding unnecessary duplication in the preparation of libraries of infrared absorption curves. Instead of distributing large infrared spectra curves, however, the data would be promulgated as coded data on I.B.M. cards and I.B.M. sorters would be used to perform the necessary matching. This program has advanced to the point where now some 25,000 infrared absorption curves, coded on I.B.M. cards are available. The cards can be obtained from ASTM and once available, a qualitative identification may consist of merely a series of sorts on I.B.M. machines. Even the slowest sorters will permit comparison of from 400 to 600 per minute.

The present-day wide spread and increasing use of infrared absorption data in the field of fatty acid chemistry by means of group frequency techniques may soon be augmented by even greater use of "fingerprint" identifications, and ASTM coded data and I.B.M. sorters will be commonplace equipment in the laboratory of the fatty acid chemist.

REFERENCES

1. O'CONNOR, ROBERT T., "Application of Infrared Spectrophotometry to Fatty Acid Derivatives," *J. Am. Oil Chemists' Soc.*, **33**, 1-15 (1956).
2. KAUFMANN, H. P., VOLBERT, F., AND MANKEL, G., "The Application of Infrared Spectroscopy to Fats, I. The Literature," *Fette, Seifen, Anstrichmittel*, **61**, 547-59 (1959).
3. JULIUS, W. H., "Bolometric Investigations of Absorption Spectra," *Verhandel. Koninkl. Akad. Wetenschap. Amsterdam*, Sect. 1, 1, No. 1 49 pp. (1892).
- 4a. SHEREVE, O. D., HEETHER, M. R., KNIGHT, H. B., AND SWERN, DANIEL, "Infrared Absorption Spectra, Some Long-Chain Fatty Acids, Esters, and Alcohols," *Anal. Chem.*, **22**, 1498-1501 (1950); 4b. "Neo-Fatty Acids," H. SOBOTKA, AND F. E. STYNLER, *J. Am. Chem. Soc.*, **72**, 5139-43 (1950); 4c. "Fatty Acids (Survey): Infrared Absorption," ROBERT T. O'CONNOR, "Encyclopedia of Chemical Technology," Vol. 6, Pages 196-9, R. E. KIRK, AND D. F. OTHMER (eds.)—Interscience Encyclopedia, Inc., New York, 1951; 4d. "The Infrared Spectra of Saturated Fatty Acids with Even Number of Carbon Atoms from Caproic, C_6 (Hexanoic), to Stearic, C_{18} (octadecanoic), and of Their Methyl and Ethyl Esters," ROBERT T. O'CONNOR, ELSIE T. FIELD, AND W. SIDNEY SINGLETON, *J. Am. Oil Chemists' Soc.*, **28**, 154-60 (1951); 4e. "The Infrared Absorption Spectra of Saturated Fatty Acids and Esters," R. G. SINCLAIR, A. F. MCKAY, AND R. NORMAN JONES, *J. Am. Chem. Soc.*, **74**, 2570-75 (1952); 4f. "The Infrared Absorption Spectra of Unsaturated Fatty Acids and Esters," R. G. SINCLAIR, A. F. MCKAY, G. S. MYERS, AND R. NORMAN JONES, *J. Am. Chem. Soc.*, **74**, 2578-85 (1952); 4g. "Infrared Spectra of Branched-Chain Fatty Acids," N. K. FREEMAN, *J. Am. Chem. Soc.*, **74**, 2523-28 (1952); 4h. "Infrared Spectra of Aluminum Soaps," W. H. HARPLE, S. E. WIBERLEY, AND W. H. BAUER, *Anal. Chem.*, **24**, 635-38 (1952).
5. HOLMAN, RALPH T., AND EDMONDSON, PAGE R., "Near-Infrared Spectra of Fatty Acids and Some Related Substances," *Anal. Chem.*, **28**, 1533-38 (1956).
6. GODDU, ROBERT F., "Determination of Unsaturation by Near-Infrared Spectrophotometry," *Anal. Chem.*, **29**, 1790-94 (1957).
7. HOLMAN, RALPH T., ENER, SIRET, AND EDMONDSON, PAGE R., "Detection and Measurement of *Cis* Unsaturation in Fatty Acids," *Arch. Biochem. Biophys.*, **80**, 72-74 (1959).
8. FENTON, A. J., JR., AND CRISLER, R. O., "Determination of *Cis*-Unsaturation in Oils by Near-Infrared Spectroscopy," *J. Am. Oil Chemists' Soc.*, **36**, 620-23 (1959).
9. CRISLER, R. O., AND BURRILL, A. M., "Determination of Hydroxyl Value of Alcohols by Near-Infrared Spectroscopy," *Anal. Chem.*, **31**, 2055-57 (1959).
10. HILTON, C. L., "Determination of Hydroxyl Numbers by Near-Infrared Absorption," *Anal. Chem.*, **31**, 1610-12 (1959).
11. HOLMAN, RALPH T., NICKELL, CHRISTENSE, PRIVETT, ORVILLE S., AND EDMONDSON, R., "Detection and Measurement of Hydroperoxides by Near-Infrared Spectrophotometry," *J. Am. Oil Chemists' Soc.*, **35**, 422-5 (1958).
12. GODDU, ROBERT F., AND DELKER, DOROTHY A., "Determination of Terminal Epoxides by Near-Infrared Spectrophotometry," *Anal. Chem.*, **30**, 2013-16 (1958).

13. CRECELIUS, S. B., KAGARISE, R. E., AND ALEXANDER, A. L., "Studies of the Mechanism of Drying Oil Oxidation, Film Formation and Degradation," presented before the Division of Paint, Plastics and Printing Ink Chemistry, Am. Chem. Soc., 126th Meeting, New York, Sept. 12-17, 1954, Am. Chem. Soc. Abs. of Papers, 26 1P (1954).
14. BAYZER, H., SCHAUBENSTEIN, E., AND WINSAUER, K., "The Infrared Spectrophotometric Determination of the Hydroxyl Content of C₁₈ Fatty Acids and Their Esters," *Monatsh.*, **89**, 15-22 (1958).
15. KABASAKALIAN, P., TOWNLEY, E. R., AND YUDIS, M. D., "Infrared Determination of Hydroxyl Equivalents in Steroids," *Anal. Chem.*, **31**, 375-6 (1959).
16. THOMAS, W. J. O., "Infrared Studies of the Molecular Interactions of Omega-Hydroxy-Palmitic Acid," *J. Chem. Soc.*, **1951**, 3307-11.
17. DAVIES, M. M., "An Infrared Study of Omega-Hydroxyundecanoic Acid in Carbon Tetrachloride," *J. Chem. Phys.*, **6**, 770-4 (1938).
18. MCCUTCHEON, J. W., CRAWFORD, M. F., AND WELSH, H. L., "The Isomeric Structure of C₁₈ Unsaturated Acids from Their Raman and Infrared Spectra," *Oil & Soap*, **18**, 9-11 (1941).
19. MORRIS, S. G., "Fat Rancidity. Recent Studies on the Mechanism of Fat Oxidation in Its Relation to Rancidity," *J. Agr. Food Chem.*, **2**, 126-31 (1954).
20. HENICK, A. S., "Determination of Deterioration Products of Autooxidized Milk Fat by Infrared Spectrophotometry," *Food Technol.*, **5**, 145-7 (1951).
21. CHANG, S. S., AND KUMMEROW, F. A., "The Isolation and Characterization of the Polymers Formed During the Autoxidation of Ethyl Linoleate," *J. Am. Oil Chemists' Soc.*, **30**, 403-7 (1953).
22. MOLAISON, L. J., O'CONNOR, R. T., AND SPADARO, J. J., "Long-Chain Unsaturated Alcohols from Jojoba Oil by Sodium Reduction," *J. Am. Oil Chemists' Soc.*, **36**, 379-82 (1959).
23. HARRISON, S. A., AND TOLBERG, W. E., "Peroxide Catalyzed Polymerization of Styrene in Pure Fatty Methyl Esters," *J. Am. Oil Chemists' Soc.*, **30**, 114-17 (1953).
24. MURPHY, J. E., AND SCHWEMER, W. C., "Infrared Analysis of Emulsion Polishes," *Anal. Chem.*, **30**, 116-26 (1958).
25. DUPUY, H. P., O'CONNOR, R. T., AND GOLDBLATT, L. A., "The Preparation and Infrared Spectra of Morpholides of Ricinoleic Acid and Some of its Derivatives," *J. Am. Oil Chemists' Soc.*, **35**, 99-102 (1958).
26. VAN TAMELEN, E. E., AND SHAMMA, M., "Assignment of the Olefinic Position in Unsaturated Acids by Means of the Iodolactonization Reaction," *J. Am. Chem. Soc.*, **76**, 2315-17 (1954).
27. RASMUSSEN, R. S., BRATTAIN, R. R., AND ZUCCO, P. S., "Infrared Absorption Spectra of Some Octenes," *J. Chem. Phys.*, **15**, 135-40 (1947).
28. SHEPPARD, N., AND SUTHERLAND, G. B. B. M., "Vibration Spectra of Some Hydrocarbon Molecules. I. Frequencies Due to Deformation Vibrations of Hydrogen Atoms Attached to Double Bonds," *Proc. Roy. Soc. London*, **196 A**, 195-216 (1949).
29. SHEREVE, O. D., HEETHEER, M. R., KNIGHT, H. B., AND SWERN, DANIEL, "Determination of Trans-Octadecenoic Acids, Esters, and Alcohols in Mixtures," *Anal. Chem.*, **22**, 1261-64 (1950).
30. PASCHKE, R. F., JACKSON, J. E., AND WHEELER, D. H., "Thermal Polymerization of Drying Oils. Isomers of Methyl Linoleate," *Ind. Eng. Chem.*, **44**, 1113-19 (1952).
31. BICKFORD, W. G., DUPRE, E. F., MACK, C. H., AND O'CONNOR, R. T., "The Infrared Spectra and the Structural Relationships Between Alpha- and Beta-Eleostearic Acids and Their Maleic Anhydride Adducts," *J. Am. Oil Chemists' Soc.*, **30**, 376-81 (1953).
32. SWERN, DANIEL, KNIGHT, H. B., SHEREVE, O. D., AND HEETHEER, M. R., "Comparison of Infrared Spectrophotometric and Lead Salt-Alcohol Methods for Determination of Trans-Octadecenoic Acids and Esters," *J. Am. Oil Chemists' Soc.*, **27**, 17-21 (1950).
33. JACKSON, F. L., AND CALLEN, J. E., "Evaluation of the Twitchell Isooleic Method: Comparison with the Infrared Trans-Isooleic Method," *J. Am. Oil Chemists' Soc.*, **28**, 61-65 (1951).
34. O'CONNOR, R. T., ET AL., "Report of the Spectroscopy Committee, 1958-59," *J. Am. Oil Chemists' Soc.*, **36**, 627-31 (1959).
35. JACKSON, J. E., PASCHKE, R. F., TOLBERG, W. E., BOYD, H. M., AND WHEELER, D. H., "Isomers of Linoleic Acid. Infrared and Ultraviolet Properties of Methyl Esters," *J. Am. Oil Chemists' Soc.*, **29**, 229-34 (1952).
36. AHLERS, N. H. E., BRETT, R. A., AND MCTAGGART, N. G., "An Infrared Study of the Cis and Trans Isomers of Some C₁₈ Fatty Acids," *J. Appl. Chem. (London)*, **3**, 433-43 (1953).

37. GAMBLE, D. L., AND BARNETT, C. E., "Infrared Absorption Spectra of Drying Oils," *Ind. Eng. Chem.*, **32**, 375-78 (1940).
38. O'CONNOR, R. T., "Infrared Absorption Spectra," *J. Am. Oil Chemists' Soc.*, **32**, 624-33 (1955).
39. CHIPAULT, J. R., AND HAWKINS, J. M., "The Determination of Conjugated *Cis-Trans* and *Trans-Trans*-Methyl Octadecadienates by Infrared Spectrometry," *J. Am. Oil Chemists' Soc.*, **36**, 535-39 (1959).
40. WHEELER, D. H., "Infrared Absorption Spectroscopy in Fats and Oils," Chapter 6, "Progress in the Chemistry of Fats and Other Lipides," Vol. 2, HOLMAN, R. T., LUNDBERG, W. O., AND MALKIN, T., eds. Academic Press, Inc., New York, 1954.
- 41a. BENEDICT, J. H., AND DAUBERT, B. F., "The Partial Hydrogenation of Triolein," *J. Am. Chem. Soc.*, **72**, 4356-59 (1950); 41b. "Hydrogenation of Methyl Beta-Eleostearate," M. L. WOLTEMAE, AND B. F. DAUBERT, *J. Am. Chem. Soc.*, **72**, 1233-40 (1950); 41c. Hydrogenation of Methylolenate. II. Studies on the Structure of the Isolinoleic Acids," D. REBELLO, AND B. F. DAUBERT, *J. Am. Oil Chemists' Soc.*, **28**, 183-85 (1951).
- 42a. FEUGE, R. O., PEPPER, M. B., O'CONNOR, R. T., AND FIELD, E. T., "Modification of Vegetable Oils. XI. The Formation of *Trans* Isomers During the Hydrogenation of Methyl Oleate and Triolein," *J. Am. Oil Chemists' Soc.*, **28**, 420-26 (1951); "XV. Formation of Isomers During Hydrogenation of Methyl Linoleate," R. O. FEUGE, E. R. COUSINS, S. P. FORE, E. F. DUPRE, AND R. T. O'CONNOR, *J. Am. Oil Chemists' Soc.*, **30**, 454-60 (1953); 42b. "Positional Isomers Formed During the Hydrogenation of Cottonseed Oil," M. H. CHAHINE, E. R. COUSINS, AND R. O. FEUGE, *J. Am. Oil Chemists' Soc.*, **35**, 396-401 (1958); 42c. "Positional Isomers Formed During the Hydrogenation of Methyl Linoleate Under Various Conditions," E. R. COUSINS, WILMA A. GUICE, AND R. O. FEUGE, *J. Am. Oil Chemists' Soc.*, **36**, 24-28 (1959).
43. BACKDERF, R. H., AND BROWN, J. B., "Nature of the Monoethenoic Fatty Acids of Butterfat," *Arch. Biochem. Biophys.*, **76**, 15-27 (1958).
44. SCOTT, W. E., HERB, S. F., MAGIDMAN, P., AND RIEMENSCHNEIDER, R. W., "Unsaturated Fatty Acids of Butterfat," *J. Agri. Food Chem.*, **7**, 125-29 (1959).
45. KUHN, H., AND LUCK, H., "The *Trans* Olefin Content of Various Naturally Occurring Fats and Its Alteration Through Ultraviolet Irradiation," *Z. Lebensm.-Untersuch. u.-Forsch.*, **109**, 306-15 (1959).
- 46a. MCCUTCHON, MARIAN A., O'CONNOR, R. T., DUPRE, ELSIE F., GOLDBLATT, L. A., AND BICKFORD, W. G., "Ricinelladic Acid and Methyl Ricinelladate. Their Preparation and Determination by Infrared Spectroscopy," *J. Am. Oil Chemists' Soc.*, **36**, 115-18 (1959); 46b. "Derivatives of Ricinelladic Acid. Their Infrared Spectra and Conformation of the Ricinelladic Moiety," *J. Am. Oil Chemists' Soc.*, **36**, 450-53 (1959).
47. MARUTA, SENIJO, AND SUZUKI, YOSHIHITO, "Reaction of Methyl Ricinoleate and *tert*-Butyl Chromate," *Kogyo Kagaku Zasshi*, **60**, 31-33 (1957).
48. KHAN, N. A., "Elaidinization; Studies on the Isomerization of Fatty Acids and Esters and Preparation of Elaidic Acid," *Pakistan J. Biol. Agr. Sci.*, **1**, 107-18 (1958).
- 49a. BAER, E., MAURUKAS, J., AND RUSSELL, M., "Synthesis of Enantiomeric α -Cephalins," *J. Am. Chem. Soc.*, **74**, 152-57 (1952); 49b. "On the Crystallization, Structure, and Infrared Spectra of Saturated *L*- α -Lecithins," E. BAER, *J. Am. Chem. Soc.*, **75**, 621-23 (1953).
- 50a. FREEMAN, NORMAN K., LINDGREN, FRANK T., NG, YOOK C., AND NICHOLS, ALEX V., "Infrared Spectra of Some Lipoproteins and Related Lipides," *J. Biol. Chem.*, **203**, 293-304 (1953); 50b. "Serum Lipide Analysis by Chromatography and Infrared Spectrophotometry," *J. Biol. Chem.*, **227**, 449-64 (1957); 50c. Infrared Spectroscopy of Serum Lipides," N. K. FREEMAN, *Ann. N. Y. Acad. Sci.*, **69**, 131-44 (1957); 50d. "Analysis of Milk Phospholipids by Chromatography and Infrared Spectrophotometry," L. M. SMITH, AND N. K. FREEMAN, *J. Dairy Sci.*, **42**, 1450-62 (1959); 50e. "Serum Phospholipide Analysis by Chromatography and Infrared Spectrophotometry," GARY J. NELSON, AND NORMAN K. FREEMAN, *J. Biol. Chem.*, **234**, 1375-80 (1959).
- 51a. SCHWARZ, H. P., "Infrared Spectra of Tissues," *Appl. Spectroscopy*, **6**, No. 4, 15-18 (1952); 51b. "Infrared Spectra of Tissues," H. P. SCHWARZ, H. E. RIGGS, C. F. GLICK, W. CAMERON, E. BEYER, B. JAFFEE, AND L. TROMBETTA, *J. Phil. Gen. Hosp.*, **2**, 136-41 (1951); 51c. "Infrared Spectroscopy of Brain Tissue. A Lipide Fraction in Normal and Irradiated Adult and Fetal Rats," H. P.

- SCHWARZ, H. E. RIGGS, C. GLICK, J. McGRATH, W. CAMERON, E. BEYER, AND E. BEW, JR., *Proc. Soc. Exptl. Biol. Med.*, **80**, 467-72 (1952); 51d. "Quantitative Infrared Spectroscopy of Desoxyribonucleic Acid in the Fractional Milligram Range," H. P. SCHWARZ, R. CHILD, L. DREISBACH, AND S. V. MASTRANGELO, *Science*, **123**, 328-9 (1956); 51e. "Infrared Studies of Tissue Lipides," H. P. SCHWARZ, L. DREISBACH, R. CHILDS, AND S. V. MASTRANGELO, *Ann. N. Y. Acad. Sci.*, **69**, 116-30 (1957).
- 52a. MARINETTI, G., AND STOTZ, E., "Studies on the Structure of Sphingomyelin. III. Quantitative Data on the Peroxide and Periodate Uptake During the Oxidation of Sphingomyelin," *J. Am. Chem. Soc.*, **76**, 1345-46 (1954); 52b. "Studies on the Structure of Sphingomyelin. IV. Configuration of the Double Bond in Sphingomyelin and Related Lipides, and a Study of Their Infrared Spectra," G. MARINETTI, AND E. STOTZ, *J. Am. Chem. Soc.*, **76**, 1347-52 (1954).
53. RENKONEN, K. O., AND KOULUMIES, R., "Serum Lipides in the Infrared Region. Spectrophotometric Study of Diabetics and Normals," *Ann. Med. Exptl. et Biol. Fenniae (Helsinki)*, **31**, 248-53 (1953).
54. HANAHAN, D. J., AND JAYKO, M. E., "The Isolation of Dipalmitoleyl-L-Alpha-Glycerolphosphorylcholine from Yeast. A New Route to (Dipalmitoyl)-L-Alpha-Lecithin," *J. Am. Chem. Soc.*, **74**, 5070-73 (1952).
55. LABAREERE, J. A., CHIPAUT, J. R., AND LUNDBERG, W. O., "Cholesteryl Esters of Long-Chain Acids. Infrared Spectra and Separation by Paper Chromatography," *Anal. Chem.*, **30**, 1466-70 (1958).
- 56a. LECOMTE, J., "The Possibilities Offered by Infrared Spectra for a Study of the Constituents of Fatty Materials. I. Oleagineux 5-685-88 (1950). II. 6-72-81 (1951). III. 6-127-36 (1951); 56b. "Infrared Spectroscopy of Fats," J. LECOMTE, I. *Fette, Seifen Anstichmittel*, **56**, 23-8 (1954). II. 100-5.
57. FAVIER, YVONNE, "Infrared Absorption of Some Vegetable Oils," *Compt. rend.*, **247**, 295-297 (1958).
58. HIRES, J., AND BALOG, JÁNOS, "Examination of Vegetable Oils by Infrared Absorption," *Magyar Kem. Fajoirat*, **60**, 50-4 (1954).
59. MINUTILLI, F., "Application of Spectrophotometry in the Study of Vegetable Oils," *Rass Chim.*, **10** (3) 24-7 (1958).
- 60a. D'ARRIGO, G., "Spectrophotometric Research of Sea Fish Oils," *Olli Minerali, Grassi E. Saponi, Colori E. Vernici*, **35**, 111-13 (1958); 60b. Spectrophotometric Detection of Fish Oils," G. D'ARRIGO, *Boll. inform. ind. olearia e saponiera*, **3**, 51-4 (1957).
61. MINUTILLI, FEDERICO, "Effect of Refining of the Infrared Spectrum of Olive Oil," *Rass chim.*, **9** (4) 13-15 (1957).
62. BOTTINI, E., AND SAPETTI, C., "Spectrometry in the Detection of Adulteration of Olive Oil," *Ann. sper. agrar. (Rome)*, **12**, 1007-44 (1958).
63. BARTLET, J. G., AND MAHON, J. H., "Identification of Oils and the Detection of Oil Adulteration by Differential Infrared Spectroscopy," *J. Assoc. Official Agr. Chemists*, **41**, 450-9 (1958).
64. EARLE, F. R., MELVIN, E. H., MASON, L. H., VAN ETEN, C. H., AND WOLFF, I. A., "Search for New Industrial Oils. I. Selected from 24 Plant Families," *J. Am. Oil Chemists' Soc.*, **36**, 304-07 (1959).
65. GLASS, CURTIS A., AND MELVIN, EUGENE H., "Determination of Composition of Vinyl Copolymers by Infrared," *J. Am. Oil Chemists' Soc.*, **36**, 100-01 (1959).
66. DUPUY, H. P., CALDERON, ROBERTO, MCCALL, E. R., O'CONNOR, R. T., AND GOLDBLATT, L. A., "The Cyanoethylation and Infrared Spectra of Some Ricinoleic Acid Derivatives," *J. Am. Oil Chemists' Soc.*, **36**, 659-63 (1959).
67. FORE, SARA P., O'CONNOR, ROBERT T., AND GOLDBLATT, LEO A., "The Reaction of Mercaptoacetic Acid with Methyl Linoleate and Linoleic Acid," *J. Am. Oil Chemists' Soc.*, **35**, 225-30 (1958).
68. PRATT, CHARLES, AND WENDER, SIMON H., "Identification of Rutin and Isoquercitin in Cottonseed," *J. Am. Oil Chemists' Soc.*, **36**, 392-94 (1959).
69. BRUNN, H. H., "Infrared Investigation of the Location of the Ethylenic Bonds in the Newly Discovered Palustic Acid," *Acta Chem. Scand.*, **11**, 907-9 (1957).
70. FUCHS, W., AND DIEBERG, R., "Solution of the Montanic Acid Problem by Chromatography and Infrared Spectroscopy," *Fette, Seifen, Anstichmittel*, **58**, 826-31 (1956).
71. JONES, R. N., MCKAY, A. F., AND SINCLAIR, R. G., "Band Progressions in the Infrared Spectra of Fatty Acids, and Related Compounds," *J. Am. Chem. Soc.*, **74**, 2575-78 (1952).
72. MEIKLEJOHN, R. A., MEYER, R. J., ARONOVIC, S. M., SCHUETTE, H. A., AND MELOCHE, V. W., "Characterization of Long-Chain Fatty

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- Acids by Infrared Spectroscopy," *Anal. Chem.*, **29**, 329-33 (1957).
73. SUSI, HEINO, "Identification of Position Isomers of Stearic Acid Derivatives by Infrared Spectroscopy," *Anal. Chem.*, **31**, 910-13 (1959).
- 74a. CORNISH, P. J., AND CHAPMAN, D., "Infrared Spectra of Some Monocarboxylic Acids," *J. Chem. Soc.*, **1957**, 1746-51; 74b. "The 720 cm^{-1} Band in the Infrared Spectra of Crystalline Long-Chain Compounds," D. CHAPMAN, *J. Chem. Soc.*, **1957**, 4489-91.
- 75a. CHAPMAN, D., "Infrared Spectra and the Polymorphism of Glycerides," *Nature*, **176**, 216-17 (1955); 75b. "Infrared Spectra and the Polymorphism of Glycerides, I. *ibid.* II. 1,3, Diglycerides and Saturated Triglycerides, *ibid.* III. Palmitodistearins and Dipalmitostearins, *ibid.* IV. Myristopalmitins and Myristostearins. D. CHAPMAN, *J. Chem. Soc.*, **1956**, 55-60; **2522-28**; **1957**, 2715-20; **1958**, 3186-8; 75c. "Infrared Spectroscopic Characterization of Glycerides," DENNIS CHAPMAN, *J. Am. Oil Chemists' Soc.*, **37**, 73-77 (1960).
76. CHAPMAN, D., CROSSLEY, A., AND DAVIES, A. C., "The Structure of the Major Component Glyceride of Cocoa Butter and of the Major Oleodisaturated Glyceride of Lard," *J. Chem. Soc.*, **1957**, 1502-9.

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FLUORIDATION OF DENTAL ENAMEL

Dental enamel is a complex substance, the composition of which is somewhat variable. X-ray diffraction experiments reveal that the structure is predominantly that of hydroxyapatite, $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. Chemical analyses reveal the presence of other elements, including Mg, Na, K, Cl, F and C, some of which may be in substitutional or interstitial solid solution within the apatite structure. In addition, organic material comprises from 2 to 4 weight per cent of dental enamel.

It has been well established by numerous controlled experiments and observations that treatment of teeth with a fluoride results in a diminished tendency toward decay. The treatment may be accomplished by putting a fluoride in the drinking water, by topical application to the teeth, or by in-

corporation of a fluoride into a dentifrice. The mechanism whereby the fluoride accomplishes its beneficial results has been the subject of considerable research without yet being explained fully. The fluoride ion may act as a poison to acid-forming bacteria, thereby decreasing the rate of formation of acid in the mouth, or the fluoride may be incorporated into the enamel structure as calcium fluoride and/or as fluorapatite, thereby decreasing the acid solubility of the enamel. Several experimental approaches, including chemical analysis, x-ray and electron diffraction, and infrared analysis, have been directed toward elucidating the latter point. In order to appreciate what contribution has been made by means of infrared, it is necessary to refer briefly to the results of chemical analyses and diffraction studies as well.

Chemical analyses have revealed that fluoride is introduced into enamel upon treatment, that the enamel of teeth in areas of relatively high fluoride content in natural water supplies contains more fluorine than in areas of low-fluoride water supplies, and that caries-resistant teeth contain more fluorine than do carious teeth. Thus the results of chemical analyses are very valuable,¹ but chemical analyses can provide no direct information on the structural form of fluoride in the enamel.

X-ray and electron diffraction techniques have established that treatment of dental enamel with fluorides does result in the formation of calcium fluoride. Much information has been obtained on the transformation of an apatite structure to a calcium fluoride structure, including the roles of such factors as the choice of fluoride reagent, its concentration, pH and time of treatment.² However, diffraction techniques can result in little or no information on the possible formation of small amounts of fluorapatite, because of the close crystallographic similarity between hydroxyapatite and fluorapatite and because the enamel pattern lacks

sharpness due both to small crystal size and to solid solution components. It has been shown that no crystallographic method can be expected to detect less than 17 per cent fluorapatite in dental enamel.³

Infrared analysis has been applied to this general area of research in two distinct ways.

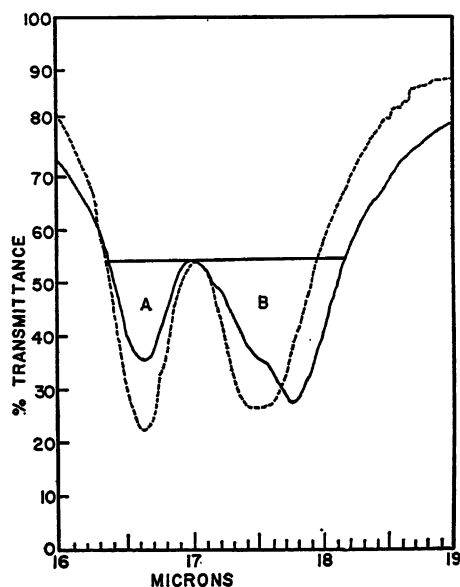
(1) Structural studies have been made by means of infrared on dental enamel itself, particularly with respect to the form of carbonate therein. Even though enamels typically contain several per cent carbonate, no calcium or magnesium carbonates are revealed by x-ray diffraction patterns of enamel. Infrared spectra, however, reveal the existence of chemical bonds identical to those in calcite and magnesite.^{4, 5} So the enamel contains carbonate rather than bicarbonate, and it is predominantly at least as calcite rather than as a carbonate-apatite. Apparently the calcite crystallites are simply too small to be revealed in the diffraction patterns.

(2) Infrared methods have been developed for the quantitative analysis of mixtures of hydroxyapatite and fluorapatite.⁶ Pressed disks of powdered sample mixed with potassium iodide are used, and the analysis is based on spectral differences in the 16 to 18 μ region. A fluorapatite band at 17.5 μ is shifted to 17.8 μ for hydroxyapatite with an accompanying difference in the relative shapes of the 16.6 and 17.5–17.8 μ bands, Figure 1. The horizontal line in Figure 1 is drawn tangent to the intersection of the two bands, and the areas are measured with a planimeter. The ratio of area B to area A is determined on known mixtures of the two apatites to prepare an empirical calibration curve. The average deviation of repeated measurements on the same disk is well under one per cent fluorapatite in the sample, and the average error for a fluorapatite determination is slightly over one per cent fluorapatite in the sample. Alternatively, a base-line technique can be used instead of the area measurement method, but the pres-

ence of calcium fluoride results in a broad absorption in the region which makes it difficult to locate a valid base-line.

Insufficient data have been obtained to evaluate fully the conditions necessary for the formation of fluorapatite by treatment of dental enamel with fluoride reagents. However, it has been shown⁷ that fluorapatite is formed on treatment with acidic sodium fluoride, that relatively little or no fluorapatite is formed on treatment with neutral sodium fluoride, and that no fluorapatite is formed on treatment with sodium silicofluoride. (The latter two conclusions are limited, of course, to the time and concentration conditions tested.)

In summary, infrared analysis has been useful in contributing to the present state of knowledge of the structure of dental enamel and of the changes wrought therein by fluoridation. Infrared techniques provide unique information which is not available via other experimental methods such as chemical analysis and diffraction of x-rays



(Courtesy American Chemical Society)

FIG. 1. Spectrum showing areas for analysis of mixtures of hydroxyapatite and fluorapatite. — Hydroxyapatite. - - - Fluorapatite.

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and electrons. Thus a maximum amount of information is obtained when several available experimental approaches are brought to bear on the problem.

REFERENCES

1. McCANN, H. G., AND BULLOCK, F. A., "Reactions of Fluoride Ion with Powdered Enamel and Dentin," *J. Dental Research*, **34**, 59 (1955).
2. FISCHER, R. B., MUHLER, J. C., AND WUST, C. J., "Effects of Several Fluoride Reagents on the Structure of Powdered Dental Enamel," *J. Dental Research*, **33**, 50 (1954).
3. TRAUTZ, O. R., "The Use of X-Ray Diffraction in Dental Research," *Norelco Reporter*, **2**, 19 (1955).
4. POSNER, A. S., AND DUYCKAERTS, G., "Infrared Study of the Carbonate in Bone, Teeth and Francolite," *Experientia*, **10**, 424 (1954).
5. UNDERWOOD, A. L., TORIBARA, T. Y., AND NEWMAN, W. F., "An Infrared Study of the Nature of Bone Carbonate," *J. Am. Chem. Soc.*, **77**, 317 (1955).
6. FISCHER, R. B., AND RING, C. E., "Quantitative Infrared Analysis of Apatite Mixtures," *Anal. Chem.*, **29**, 431 (1957).
7. RING, C. E., "Some Physical and Chemical Methods in the Study of The Dental Enamel-Fluorapatite System," Dissertation, Indiana University, Bloomington, Indiana (1956).

ROBERT B. FISCHER

GAS CHROMATOGRAPHY IDENTIFICATIONS BY SPECTROGRAPHY. See GAS CHROMATOGRAPHY IDENTIFICATIONS, p. 605.

HISTORY*

In 1800 William Herschel¹ discovered infrared radiation by placing a thermometer at successive points in a glass prism dispersed spectrum of the sun and observing the temperature rise. It is interesting to note that this first infrared spectrometer had the same elements as the more modern infrared instrument—a hot source of continuous radiation, prism dispersion, and a

temperature sensitive device as a detector. This new "heat" radiation was first thought to be fundamentally different from "light" radiation, but the identity of the two was generally accepted by 1840.

Progress in the infrared field was painfully slow because of the difficulty of radiation detection and characterization. In the latter half of the century the development of bolometers, thermopiles and radiometers combined with galvanometers provided adequate radiation measurements. These, combined with grating or interferometric wavelength measurements and an understanding of black body emission laws, permitted an enlightened approach to experimental infrared by 1900.

In the decade 1900–1910, a magnificent research program by W. W. Coblentz² provided evidence of the chemical value of infrared. Coblentz obtained absorption spectra of many organic liquids as well as absorption, emission, and reflection spectra of a large number of inorganics. Some empirical correlations of infrared absorption and molecular structure were noted but the fundamental relationship was not perceived and chemical possibilities were not realized. Instead, the main application for infrared was in academic physics research. With the observation of rotational absorption structure in 1913, and the concept of the vibrating molecule in 1916, the study of molecular quantum mechanics became of intense interest. This type of work, the use of infrared absorption spectra in fundamental calculation of molecular structure, chemical bonds, and thermodynamic constants still constitute an active field for physicists and physical chemists. Excellent texts are available covering the theoretical aspects of infrared.^{3, 4}

In the thirties, organic chemists began to consider infrared as a possible tool for material identification and functional group analysis. In 1935 there began the construction of infrared spectrometers in the research laboratories of a few larger chemical companies.

* Source: "Introduction to Infrared Spectrometry," Volume 1, compiled by Perkin-Elmer Corp., Norwalk, Conn., 1952.

Work with these instruments led to an interest in using the method for organic quantitative analysis.

The major industrial impetus came to the field early in the war when it was shown that infrared offered a rapid, accurate method⁵ of analyzing the C₄ hydrocarbon fraction of interest in the production of synthetic rubber. In answer to this interest, commercial production of infrared spectrometers was started in 1943 and 1944. The combination of instrument availability and chemical possibilities has made the infrared field an exceptionally active one since that time. Instrumentation has improved so that a range of models is available for dependable, convenient operation. The infrared instrument has, in this short time, attained such acceptance by the chemist that it is considered standard laboratory equipment in the same sense as a gravimetric balance or distillation column.

An inherent difficulty in such rapid growth is the consequent lack of applied textbooks describing instrumentation and application. Background information can be obtained from references 6-10.

REFERENCES

1. HERSCHEL, W., *Phil. Trans*, **90**, 284, 437 (1800).
2. COBLENTZ, W. W., Bull. No. 35, Carnegie Inst. Publ. (1905). Washington, D. C.
3. WU, T., "Vibrational Spectra and Structure of Polyatomic Molecules," (National University of Peking, 1939).
4. HERZBERG, G., "Infrared and Raman Spectra of Polyatomic Molecules" (D. Van Nostrand Company, Inc., New York, 1945).
5. BRATTAIN, R. R., RASMUSSEN, R. S., AND CRAVATH, A. M., *J. App. Phys.*, **14**, 418 (1943).
6. WILLIAMS, V. Z., *Rev. Sci. Inst.*, **19**, 135 (1948).
7. HARRISON, G. R., LORD, R. C., AND LOOFBOUROW, J. R., "Practical Spectroscopy," Prentice-Hall, Inc., New York, 1948.
8. Symposium, "The application of infrared spectra and chemical problems," *Trans. Faraday Soc.*, **41**, 171 (1945).
9. RANDALL, H. M., FUSON, N., FOWLER, R. G., AND DANGL, J. R., "Infrared Determination of Organic Structures," D. Van Nostrand, Inc., New York, 1949.
10. BARNES, R. B., AND GORE, R. C., *Analytical Chemistry*, **21**, 7 (1949).
- GORE, R. C., *ibid.*, **22**, 7 (1950).
- GORE, R. C., *ibid.*, **23**, 7 (1951).
- GORE, R. C., *ibid.*, **24**, 8 (1952).

PERKIN-ELMER CORPORATION

IMBEDDING-WINDOW METHOD FOR SAMPLING

The imbedding-window method for infrared sampling represents one of the most useful techniques introduced to infrared analysis. The sample to be analyzed is finely-ground, and mixed with a powdered alkali halide which does not exhibit discrete absorption peaks over the range of the infrared spectrum to be measured. The powdered mixture is then pressed into a pellet, or "window." When the window is placed in the sample beam of the infrared spectrophotometer, the absorption peaks that result are due to the imbedded sample alone.

This method has many advantages over other methods of sampling solid materials, including the use of a deposited film on alkali halide optical window "blanks," or the use of a mulling agent such as Nujol or hexachlorobutadiene. Another advantage is that there are no interfering absorption bands in the spectrum, as would arise from a mulling agent, since the alkali halide matrix materials used, being ionic, have no discrete absorption bands in the primary infrared wavelength region. Also, light transmission of the imbedding window, as shown by its recorded spectrum, is better than can usually be obtained with a film, since light scattering is reduced by the use of the window, particularly at the shorter wavelengths less than 5 microns. Quantitative analyses are readily performed with a higher precision than is obtainable with mulls or films, since an accurate measurement may be made of the weight ratio of sample to alkali halide in the window—indicating the amount of sample

that subtends the sample beam—and useful absorptivity values for specific peaks may thereby be obtained. After analysis, the windows containing the samples may be conveniently stored for future reference, over periods of time. Also, samples that are water-insoluble may be readily recovered from the window after the spectra have been obtained.

Imbedding windows with suitable optical characteristics may be readily prepared through use of proper techniques. The matrix material to be used, besides producing no discrete absorption bands, should also be preferably non-hygroscopic, easily obtainable in the pure state, and have a relatively low sintering pressure so that excessive force is not needed to press the windows. Of the alkali halides, potassium bromide and potassium chloride are both favorable, but potassium bromide is commonly used—over the wavelength region 2 to 25 microns—as it does not absorb in this region; for measurements at wavelengths longer than 25 microns, use may be made of cesium iodide and cesium bromide, both of which are transparent at wavelengths up to 50 microns. To produce a window having a diameter of one-half inch, one hundred milligrams powdered potassium bromide are mixed thoroughly with the finely-ground sample (0.05 to 0.5 milligrams), and the mixture is placed within the pressing chamber of the pressing mold, and contained by the polished surfaces of the top and bottom pressing dies. Windows are usually pressed in a pressing mold, in which a passageway has been drilled from the outer surface, through the barrel of the mold into the pressing chamber within. This is done so that during the pressing, provision may be made for removal of air that is entrapped in the powdered matrix; otherwise, when pressure is removed from the die, expansion of the entrapped air would cause clouding, and even fracture, of the window. To remove entrapped air, pressure is applied until the powder is barely impacted. Vacuum is then

applied for one-half minute by connecting the passageway in the mold to a source of vacuum. (A vacuum of 15 mm mercury, obtainable with an ordinary water aspirator, is sufficient, although use of a vacuum oil pump removes the air more quickly.) The pressing force is quickly increased to a maximum; the maximum force necessary to produce a clear window will depend on the size of the window, and can be determined by experiment—for a half-inch window containing one hundred milligrams KBr, a maximum pressing force of 20,000 pounds, a pressure of approximately 100,000 pounds per square inch, is usually sufficient. The vacuum and maximum pressure are maintained for one minute. Vacuum is then released, pressure removed, and the window removed from the pressing mold.

The thin, circular KBr window should be without cracks, and should have optically smooth faces. A window "blank," containing potassium bromide but no sample, should appear virtually transparent to the eye, the transparency being retained with time except for a slight degree of clouding, and the "blank" transmitting 85 to 90 per cent of the incident light beam for wavelengths of 2 microns and longer (addition of sample to the window may slightly lower this "baseline" transmission). By standardization of procedure, successive windows can be produced the transmission curves of which coincide within one or two per cent transmission units.

Some plastic flow of the powder takes place during pressing, but although transparent, the pressed window does not represent a case of a solid solution. Rather, the KBr in the window is pressed into a mosaic of closely-packed grains, in order that the smaller particles may be keyed and wedged into spaces between the larger grains, thus reducing the amount of interparticle air-space within the window. This results in less light-scattering at the particle interfaces within the window and, therefore, a higher

transmittance. (For this reason, KBr powder with a range of particle sizes, say, from 80 to 300 mesh, has advantages over powder composed of one mesh size only, such as 250 or 300 mesh.)

Size and sample content of windows may be greatly varied, depending on the particular application to specific analyses. Thus, windows have been pressed with diameters as large as one inch, and containing one-half gram of KBr and several milligrams of sample (necessitating a higher pressing force than that for the smaller windows), and conversely, for some micro analyses, windows have been prepared containing only 40 milligrams KBr, and fractional milligram quantities of sample. For such micro-windows, lens beam condensing units are conveniently attached to the spectrophotometer in order to concentrate the incident light beam on the small face of the window. Efficient measurement of micro samples would also result if the window were pressed in a mold which had rectangular pressing dies, so that the rectangular window resulting would more closely approximate the size of the slit image of the spectrophotometer.

When the spectra of the sample to be analyzed has many sharp, discrete absorption peaks, particular care must be taken to attain smaller particle size and adequate dispersion of the sample in the window, in order to prevent possible light scattering, and the tendency of the absorption peaks to broaden and adjacent peaks to merge. In addition to the use of motor-driven mechanical vibrators, which deliver as many as 200 crushing impacts per second, to grind and mix the sample and KBr powder, good sample dispersion has been obtained by means of dissolving the sample in a suitable solvent, spraying the solution over the KBr powder, and allowing the solvent to evaporate. A more complicated procedure, which has been utilized with some organic samples when sub-microscopic sample particles were desired for highly accurate quantitative anal-

yses, consists of cooling solutions of weighed amounts of sample and KBr rapidly in a mixture of acetone and Dry ice, followed by freeze-drying of the solidified mixture of sample and KBr, followed by vacuum drying; such freeze-drying methods can produce sample particles with diameters as small as 0.01 micron.

In the use of the imbedding window, certain limitations exist, including those that are inherent in the sampling of solid materials. Thus, if the unit cell of the sample contains strong intermolecular forces, such as may occur in highly polar compounds, the spectra may be appreciably modified from those which would be obtained from the rotationally restricted molecule in free space. In the process of window pressing, some degree of specific orientation of the sample can occur, and the alteration or elimination of one or more absorption bands could then occur if the electric vectors associated with the various group vibrations happened to lie parallel to the radiation beam. The absorptivity of individual absorption bands is also affected by the sample particle sizes and their distribution across the cross-section of the light beam, so for accuracy of quantitative analyses, uniformity in the method of sample grinding and mixing should be maintained.

Chemical nature of the sample and of KBr may also introduce errors. Because of the hygroscopic nature of KBr, the adsorbed water in the matrix powder can sometimes form hydrates of the sample, or cause hydrolysis of the sample, thus causing changes in the spectra. Moreover, KBr and KCl are not completely inert, and double decomposition may sometimes take place between halide and sample. Also, if the sample is a strong oxidizing agent, some degree of oxidation of the matrix material may occur.

Further precautions must be taken with mechanical vibrators that are often used in grinding and mixing the sample and matrix, since a rigorous grinding in the preparation of the window can sometimes cause breakdowns

in crystal structure of the sample, resulting in broadening or elimination of absorption peaks such as occur when a material has been rendered amorphous. This effect is more apt to occur in materials that have low lattice energies. In addition, excessive grinding can cause changes in the spectra due to polymorphic changes in the sample, particularly for materials that have their more stable states under the vigorous grinding conditions of window preparation. The KBr matrix may also introduce error, as the intensity of the weak absorption band that occurs near a wavelength of 9 microns in the spectrum of a window made from reagent grade KBr may increase greatly under conditions of excessive grinding, and consequently interfere strongly with the spectra of the sample. These effects are minimized if the sample and KBr are not subjected to a vigorous and prolonged grinding in a mechanical vibrator.

When the necessary precautions are observed in the preparation and application of the imbedding window method, it can be of much use, and the method has accordingly been established among infrared techniques as a basic procedure in the analysis, both qualitative and quantitative, of the widest variety of organic and inorganic solid materials.

REFERENCES

1. BAKER, A. W., *J. Phys. Chem.*, **61**, 450 (1957).
2. BAKER, S. A., BOURNE, E. J., WEIGEL, H. AND WHIFFEN, D. H., *Chem. & Ind. (London)*, **1956**, 318.
3. BROWNING, R. S., WIERLEY, S. E., AND NACHOD, F. C., *Anal. Chem.*, **27**, 7 (1955).
4. FARMER, V. C., *Chem. & Ind. (London)*, **1955**, 586.
5. LANE, T. J., SEN, D. N., AND QUAGLIANO, J. V., *J. Chem. Phys.*, **23**, 1855 (1954).
6. LEJEUNE, R., AND DUYCHAERTS, G., *Spectrochimica Acta*, **6**, 194 (1954).
7. MILKEY, R. G., *Anal. Chem.*, **30**, 1931 (1958).
8. ROBERTS, G., *Anal. Chem.*, **29**, 911 (1957).
9. ROSENKRANTZ, H., *Methods of Biochem. Anal.*, **5**, 407 (1957).

10. SCHEIDT, U., *Naturforscher*, **7b**, 270 (1952).
11. STIMSON, M. M., AND O'DONNELL, M. J., *J. Am. Chem. Soc.*, **74**, 1805 (1952).
12. WEISSBERGER, A., "Chemical Applications of Spectroscopy," Interscience Publishers, New York, 1956.

ROBERT G. MILKEY

INFRARED ABSORPTION, BASIS OF*

A basis for appreciation of infrared spectrometric applications is an understanding of the interaction between infrared radiation and matter—the absorption of infrared light by a sample. The explanation given below suffers some inaccuracies from over-simplification but permits a logical relationship between the fundamental phenomenon and its usefulness.

Electromagnetic Radiation—The Infrared Spectrum. Infrared radiation is a portion of the "electromagnetic spectrum." All the familiar types of radiation: x-rays, visible light, infrared, radiowaves, etc., are qualitatively identical in that they are light energy waves moving in accordance with the law $\lambda \nu = c$ where λ is the wavelength of the light in cm, ν is the frequency in cycles per second, and c is the velocity of light (3×10^{10} cm per second.) These radiations are differentiated by the methods used for producing and measuring them as well as their interaction with matter.

Two interchangeable units are used to describe a position in the infrared range of the electromagnetic spectrum. These are a wavelength (λ) unit, the micron (μ), $1 \mu = 10^{-4}$ cm = $10^4 \text{\AA}$; and a so-called frequency or wavenumber (ν) unit, waves per cm, which is written as cm^{-1} . A simple reciprocal relationship exists between these units, namely,

$$\nu (\text{cm}^{-1}) = \frac{1}{\lambda (\text{cm})} = \frac{10^4}{\lambda (\mu)}$$

Although this duality makes for a somewhat

* Source: "Introduction to Infrared Spectrometry," Volume 1, Perkin-Elmer Corp., Norwalk, Conn., 1952.

confusing situation, those working with infrared have not been able to agree on a common unit—they must become familiar with both in order to appreciate the literature.

The so-called frequency unit ν (cm^{-1} or waves per cm) is used because it is a more manageable number than the more fundamental unit of true frequency $\bar{\nu}$ (cycles or waves per second). From the above expressions it can be seen that $\bar{\nu}(\text{sec}^{-1}) = c\nu$. The primary region of fundamental infrared interest is the range $\bar{\nu} = 12 - 0.6 \times 10^{13}$ cycles per second, $\nu = 4000 - 200 \text{ cm}^{-1}$, $\lambda = 2.5 - 50 \mu$. The region between this and the visible $0.7\text{--}2.5 \mu$ is called the overtone or near infrared, while the region beyond 50μ is spoken of as the far infrared.

Also, for this illustration, it is desirable to consider electromagnetic radiation as a traveling field of electric force whose direction (the direction in which it would impel an electrically charged particle) oscillates with the characteristic frequency.

The Vibrating Molecule—Classical Model. The concept of the vibrating molecule is presented as a mechanical model. A model of any molecule such as HCl, CH_4 , benzene, etc., can be made by (1) taking masses, such as ball bearings, whose weights are proportional to the atomic weights of the atoms, (2) arranging them in space according to the actual space geometry of the molecule, and (3) connecting the masses by simple mechanical springs the strengths of which are proportional to the chemical bond forces. Such models of simple molecules are shown in Figure 1.

If such a model is suspended in space and struck a blow, the weights will appear to undergo random chaotic motions. However, if the model is observed with a variable frequency stroboscopic light, certain light flash frequencies will be found at which the model weights appear to stand still. The model is undergoing a series of definite frequency periodic motions and it is the sum of these motions occurring simultaneously which presents the chaotic pattern observed in steady light. A study will show that the general model of N weights will have $3N-6$ such definite frequency motions or *characteristic vibrations*.

This same model of known weights, springs, and space geometry can be analyzed mathematically by the standard equations of mechanics. Such an analysis will give the same results as the empirical approach, namely, $3N-6$ *characteristic vibration frequencies* the values of which are a function of the original knowns: weights, geometry, and springs.

If one substitutes in these equations the actual molecule data, atomic weights, interatomic distances and angles, and chemical bond forces, one finds that the resultant mechanical molecular frequencies will fall in the range $12 - 0.6 \times 10^{13}$ cycles per second, the same frequency range as infrared radiation.

The Dipole Moment. A further characteristic of a molecule which should be appreciated (although its understanding is not vital to the exposition) is the dipole moment. The atoms of a molecule carry a positive or

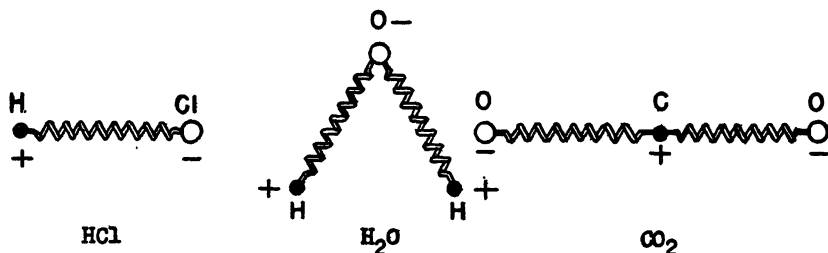


FIG. 1

INFRARED SPECTROPHOTOMETRY

negative charge. The dipole moment is a vector product, formed by concentrating the positive and negative charges at their respective electrical centers of gravity and drawing a line between them. The position of the charges vary as the atoms undergo the characteristic vibrations. Hence, a molecule can have one value for its dipole moment at one extreme of a vibration and another at

the other extreme. If these two extreme values are different, there is said to be a *change in dipole moment* associated with that characteristic frequency or vibration. If these two values are the same, there is no change in dipole moment. This is illustrated by the three characteristic vibrations of CO_2 , shown in Figure 2. Row A is the average configuration of this linear molecule; B and C are the

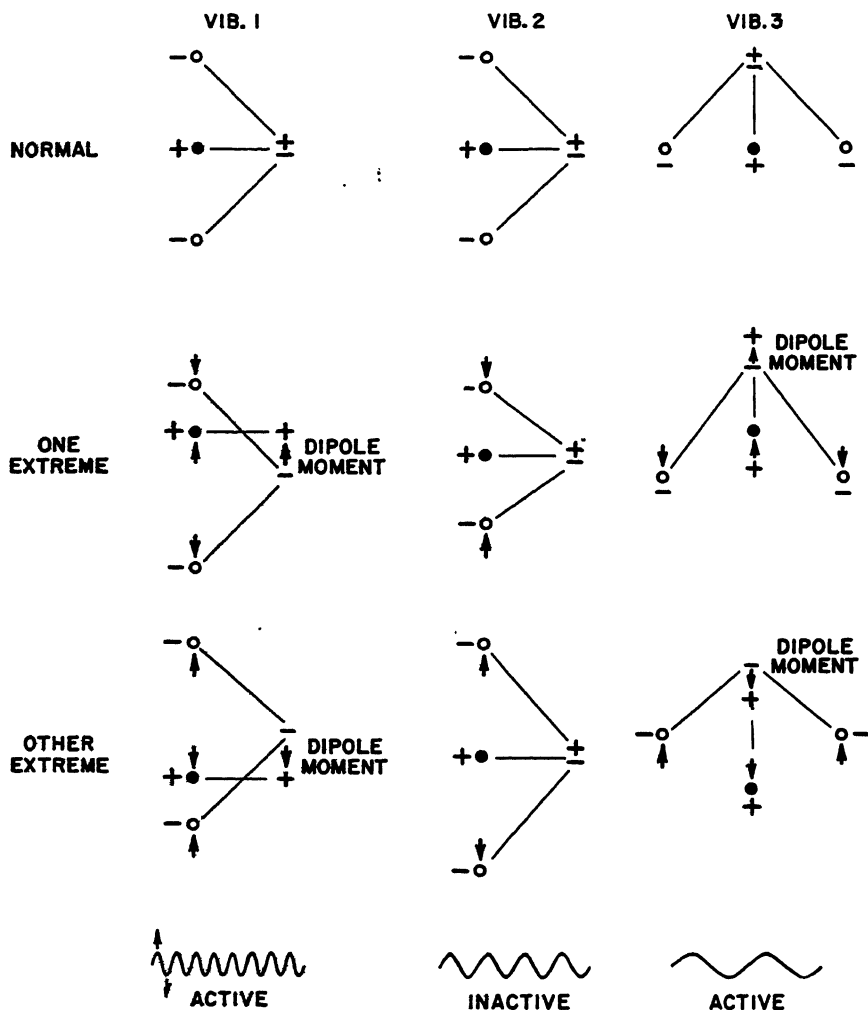


FIG. 2. Characteristic vibrations of CO_2 molecule.

For each vibration the equilibrium position is shown in the top row and the two extreme vibrations with resultant dipole moment changes in the second and third rows. The characteristic vibrations frequencies are: 1. 7×10^{13} cycles per second, 2349 cm^{-1} . 2. 4.2×10^{13} cycles per second, 1338 cm^{-1} . 3. 2×10^{13} cycles per second, 667 cm^{-1} .

two extremes. The normal molecule has no dipole moment since the charges are balanced. Vibrations 1 and 3 show a change in dipole moment associated with the motion; vibration 2 remains in balance so there is no change.

Interaction of Radiation and Molecule. If infrared radiation of successive frequencies (or wavelengths) is incident on a molecule, there will be radiation frequencies which correspond to the characteristic molecular frequencies in value. Under such natural resonant conditions, energy can be exchanged from one system to the other provided a linkage or coupling is available. The coupling mechanism is the change in dipole moment discussed above. (In a comparable system of bringing a vibrating tuning fork near another fork of the same frequency, energy is exchanged through the coupling mechanism of the air.)

In Figure 2, the oscillating electric field of the radiation tends to alternate the charge distributions in just the manner illustrated by the change in dipole moment. In so doing, the molecule is caused to vibrate, energy is exchanged from the radiation to the molecule, and the radiation is weakened or absorbed. This energy of molecular vibration is changed to translational energy by collision with a neighboring molecule, and the molecule reverts to its initial state for another radiation absorption. The translational energy appears as a temperature rise of the sample and this is the basis of infrared heating.

In short, the scanning of a molecular sample with successive infrared frequencies shows values for which the radiation is weakened or absorbed, and these values correspond to mechanical vibration frequencies of the molecule. *The infrared spectrum*, therefore, is an analysis of the molecular vibrations, and the means of obtaining this analysis, the infrared spectrometer, can be considered an infrared stroboscope playing the same role as the stroboscope used in studying the mechanical model.

This simplified picture can be extended to explain the rotational absorption effects as a modulation of the vibrational frequencies. However, the energy level aspects of the quantum mechanics give a much truer picture, and references (3) and (4), listed under "History," are suggested for further study.

PERKIN-ELMER CORPORATION

INSTRUMENTATION*

The Dispersion Instrument

The function of the dispersion instrument is to supply an infrared absorption spectrum of a sample by irradiating a sample with successive frequencies (wavelengths) of infrared light and measuring the degree to which the sample absorbs the light.

A schematic diagram of an infrared double-pass spectrometer for such a purpose is shown in Figure 1. Infrared radiation from a source S_0 is focused by M_1 and M_2 on the entrance slit, S_1 , of the monochromator. The radiation beam from S_1 (Path 1) is collimated by the off-axis paraboloid M_3 and a parallel beam traverses the prism Pr for a first refraction. It is reflected by the Littrow mirror M_4 through Pr for a second refraction and focused by the paraboloid (Path 2) at the corner mirror M_5 . The radiation returns along Path 3, traverses the prism again and back along Path 4 for reflection by M_7 to the exit slit S_2 . By this double dispersion means the radiation is spread out along the plane of S_2 . The frequency interval which passes through S_2 is focused by M_8 and M_9 on the thermocouple TC. The beam is chopped by CH near M_6 to produce an a.c. voltage at the thermocouple which is proportional to the radiant power or intensity of the beam. This voltage is amplified and recorded by an electronic potentiometer. Motor driven rotation of M_4 causes the infrared spectrum to pass across

* Source: "Introduction to Infrared Spectrometry" Volume 1, Perkin-Elmer Corp., Norwalk, Conn., 1952.

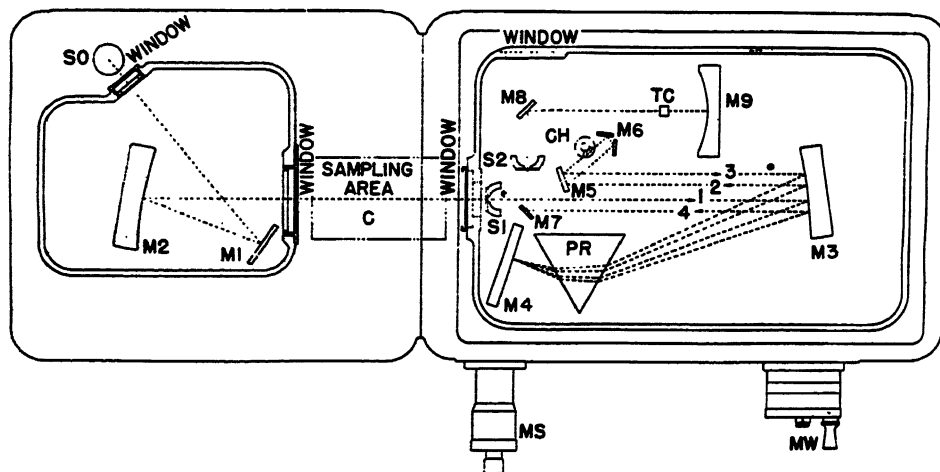
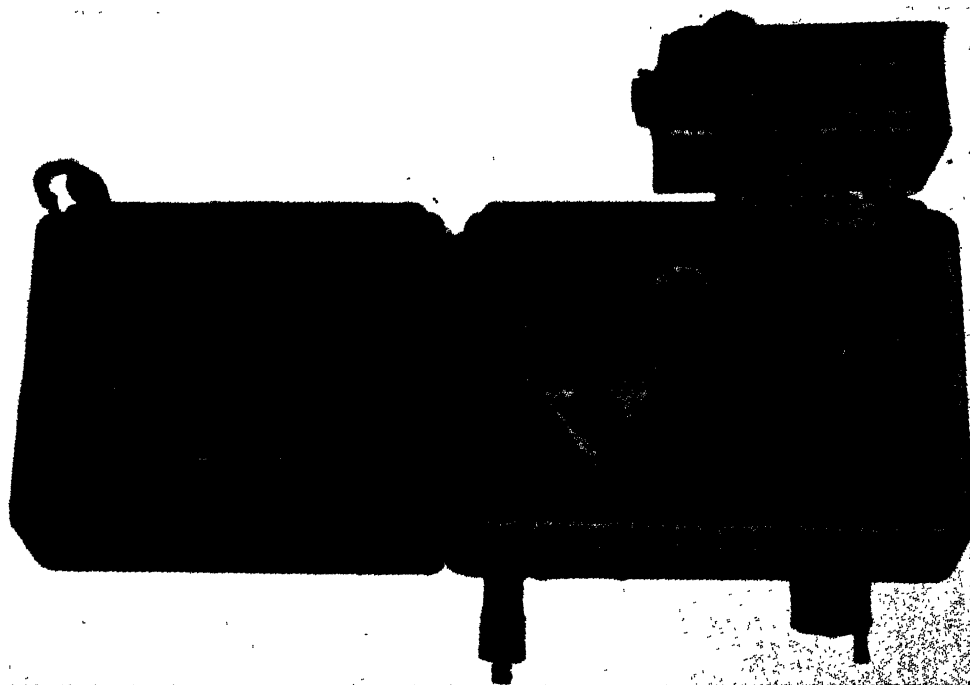


Fig. 1. Optical path of Model 112 single-beam infrared spectrometer with double-pass monochromator.

S_2 and the intensity of successive frequencies is measured.

In a single-beam instrument such as this, the radiation spectrum from the source alone is first measured, then a sample is introduced in the sample area and the source radiation

as modified by the sample is measured. A comparison of these two measurements as a function of radiation frequency provides the sample absorption in absolute terms.

A detailed discussion of an infrared spectrometer is best carried out in six sections—

source, dispersion, detection and amplification, method of photometry, recording variables and sampling.

The Infrared Source. The ideal infrared source is a black body radiator obeying Planck's law. The best approximation to the ideal is a heated cavity, but this is not generally used because of its bulk and wattage requirement. The most common sources are the globar, a bonded silicon carbide rod, and the Nernst glower, a bonded mixture of rare earth oxides in rod form. These are electrically heated to temperatures in the range 1200–2000°K. These are practical approximations to a black body as shown by their emission curves, and seem to obey Wien's displacement Law,

$$\lambda_{\max}(\mu)T(^{\circ}\text{K}) = 2900 \quad (1)$$

For the temperature range shown above, the emission maxima are from 1.5 to 2.5 μ . The desiderata of a source are stability and high emission, i.e., high temperature. A study of typical black body emission curves vs. temperature range shows that increase in T increases the short wavelength radiation much more than the long wavelength that is more generally used. For long wavelength studies, therefore, the scattered or false radiation contribution increases faster than the time radiation desired. This difficulty can be partially overcome by the use of selective filters or shutters and can be almost completely removed by the double-pass system.¹⁸ For some studies, such as infrared microscopy, where maximum intensity is necessary in spite of disadvantages, the carbon arc is used.¹

Dispersion. Dispersion defines the extent to which successive frequencies of radiation are separated or spread out in space. It can be measured as an angular separation $d\lambda/d\theta$ or a space separation at exit slit $d\lambda/dx$. The common methods of dispersion are the refraction prism and the diffraction grating. Higher dispersion can be obtained from a grating but it is usable only over a short

spectral range and in the infrared requires a fore prism for elimination of higher order diffraction. In spite of its lower dispersion, the prism instrument is more generally used because of its greater range and simplicity.

The dispersion characteristics give the wavelength distribution at the exit slit. The frequency or wavelength interval which passes out the exit slit is determined by the widths of the two slits. In prism infrared spectrometers the two slits have the same mechanical width for maximum efficiency. The primary criterion used here is the *spectral slit width* ($\Delta\nu$) or ($\Delta\lambda$) which is half the total interval falling on the exit slit. *Spectral slit width* is a better criterion than total interval because it also defines the spectral separation of two essentially monochromatic bands which can just be resolved, i.e., measured as two separate bands.

The relation between spectral slit width and single-pass Littrow monochromator characteristics is given by the formula:

$$\Delta\nu(\text{cm}^{-1}) = \nu^2 \frac{[1 - n^2 \sin^2(\alpha/2)]^{1/2} s}{4 \sin(\alpha/2)(dn/d\lambda) f} + F(s) \frac{\nu}{2b(dn/d\lambda)}, \quad (2)$$

or

$$\Delta\lambda(\text{cm}) = \frac{[1 - n^2 \sin^2(\alpha/2)]^{1/2} s}{4 \sin(\alpha/2)(dn/d\lambda) f} + F(s) \frac{\lambda}{2b(dn/d\lambda)}; \quad (3)$$

where

ν = radiation frequency in cm^{-1}

or

λ = radiation wavelength in cm

n = index of refraction of the prism at frequency ν

α = prism apex angle

$dn/d\lambda$ = dispersion of prism at frequency ν

s = mechanical slit width in cm

f = focal length in cm

b = effective prism base in cm

INFRARED SPECTROPHOTOMETRY

TABLE 1. CHARACTERISTICS OF VARIOUS PRISM MATERIALS USED IN THE INFRARED

As window materials the long wavelength limit can be extended 1-2 μ .

Material	Apex Angle	Resistance to Water Vapor	Recom- mended Range	Usable Range
			Microns	Microns
Glass	60°	Excellent	0.3-2	0.3-2
Quartz	60°	Excellent	0.3-2.5	0.2-3
LiF	72°	Good	0.2-6	0.2-6
CaF ₂	67°	Good	0.2-9	0.2-9
NaCl	60°	Poor	2-15	0.2-17
KBr	60°	Very poor	12-25	0.2-25
CsBr	55°	Very poor	15-38	—

$F(s)$ is a function approximately 0.9 for $s = 0$ and decreasing to approximately 0.5 for a value of s such that the first term equals

$$\frac{\nu}{2b \frac{dn}{d\lambda}}$$

The term

$$\frac{\nu}{2b \frac{dn}{d\lambda}}$$

is the Rayleigh term for a single-pass Littrow instrument and results from the diffraction pattern of an infinitely narrow slit. This value (actually 0.89 times the value) is the limiting spectral resolution that could be obtained if an infinite amount of spectral radiation were available. Actually, resolution about 1.5 the Rayleigh value can be obtained from a good instrument, but normally operation is conducted at spectral slit widths two or three times this value.

Table 1 gives a list of common dispersion prisms showing apex angles and normally used spectral regions. The long wavelength limit is set by prism absorption and the shorter by experimental circumstances such as light scattering or limited dispersion. In the infrared region attainable spectral slit width improves (gets smaller) toward longer wavelength because of increasing dispersion and then falls off since prism absorption requires wider slits to provide sufficient intensity for measurement. NaCl is the most

widely used prism with CaF₂ and KBr next, although CsBr may supplant KBr because of its greater transmission range.

Another characteristic evaluation of a dispersion monochromator is of value for comparing instruments of different dimensions. This criterion is the radiant power per spectral slit width at frequency ν and is given by

$$E_\nu = \frac{I\nu h D A \alpha}{f} \quad (4)$$

where

$I\nu$ = radiant power incident on entrance slit

h = the slit height

D = the angular dispersion

A = the absolute aperture (the effective area of the prism face projected on the collimator)

f = the focal length

α = monochromator efficiency (allowance for reflection losses, prism absorption, etc.)

For an infrared instrument in good condition used in a region of negligible prism absorption, $\alpha = 0.75$. Such a comparison is valid for the monochromator portion only. For the instrument as a whole, such factors as source intensity, detector efficiency, optical quality, etc., must be considered.

Detection—Amplification. *Detectors:* The most commonly used infrared detectors are thermal in type: the thermocouple, the bolometer, and the more recently introduced pneumatic cell. In a thermal detector it is necessary to differentiate signal changes caused by ambient temperature from those caused by radiation. This is done by chopping the radiation beam at a frequency (5-15 cycles/second) and measuring the a.c. signal at this frequency. This requires a detector with a short response, a difficult requirement because heat transfer is not a rapid process.

The following consideration based on a thermocouple gives an idea of the problem. Radiation is incident on the radiation re-

ceiver at a rate of J watts, is absorbed, and causes an increase in temperature. Heat energy is lost from the thermocouple through convection, radiation, and conduction at a rate of L watts per $^{\circ}\text{C}$. In time, equilibrium will occur such that $J = L\Delta T$ where ΔT is the temperature rise. If Q volts per degree is the thermoelectric coefficient of the thermocouple material, the voltage is given by

$$E = Q\Delta T = QJ/L \quad (5)$$

The response time τ (the time to reach 67 % of equilibrium value) is given by

$$\tau = C/L \quad (6)$$

where C is the heat capacity of the receiver.

The desiderata for sensitivity (high voltage) are high Q and small L , and for short response, small C and large L . The influence of L is opposed in these two requirements and a best compromise value is sought. Q is maximized by choice of materials, and C is minimized by making the receiver as small as possible and still receive the optically reduced image of the exit slit.

These expressions govern the sensitivity of the detector but the important criterion is the *noise equivalent input*, i.e., the amount of incident radiant power which will give a voltage signal equal to the inherent noise. This inherent noise (Johnson noise) is proportional to the square root of electrical resistance which, in turn, is related to the thermal conductivity. All these factors must be considered in detector design. References to the detectors commonly used are pin type thermocouple,² wire thermocouple,³ bolometer,⁴ and Golay pneumatic detector.⁵ Comparison of these various detectors is very difficult from design data and is best done by measuring each in the same radiant beam. However, some very rough noise equivalent figures for a thermocouple (measurable limits) are as follows

$$\Delta T = 10^{-4}^{\circ}\text{C}, \quad \Delta J = 10^{-11} \text{ watt}, \quad \Delta E = 10^{-9} \text{ volt}.$$

The efficiency of conversion of radiant power

to electrical power under these conditions is less than 10^{-6} . The thermal detector is essentially a heat engine and it is this low level inherent inefficiency which makes infrared instrumentation difficult.

A detector of greater efficiency is the photoconductive cell.⁶ However, its present long wavelength sensitivity limit seems to be about 5μ so that its value is limited to special applications.

Amplification: The primary use of electronics is in amplifying the small signals which arise from the various radiation detectors. This is inevitably a problem of achieving good signal-to-noise ratio so that fundamental data of the spectrum are not obscured by noise. Although special techniques are required for low noise level amplification, these are now quite well established. Much has been learned from similar low level problems in medical research, geophysical equipment and radar circuits.

The greatest attention in a low level amplifier has to be paid to the first stage, commonly called the "preamplifier." Here various forms are appropriate depending on the detector and its impedance level. The thermocouples and thermopiles are in the low impedance category and it is possible to achieve voltage amplification from modulated signals with a well-shielded transformer. For photomultipliers (and Golay cells), lead sulfide cells, and similar detectors, the impedance level is higher and so the signal is usually fed directly to the grid of the vacuum tube.

Following the preamplifier there are usually several stages of vacuum tube amplification. Here the signal level is high and so the stages are of conventional design.

The output requirements of the signal amplifier are determined by the nature of the load which is to be used. Often for modulated signals this is some form of a rectifier followed by a filter. This filter determines the bandpass and thus the noise of the system. Usually, this filtering is adjustable since

heavy filtering can be used only at low scanning speeds without deterioration of the spectra.

The requirements of the signal amplifier depend a great deal on the form in which the spectral data are obtained. Some systems operate on the null principle in which a reference beam of radiation is attenuated until no a.c. signal arises from the detector.⁷⁻⁹ In such a system, the requirements on linearity in regard to both phase and amplitude are not severe. In other systems, such as the Halford-Savitzky system,¹⁰ data are carried as the phase angle of an a.c. voltage. Here it is very important that, regardless of amplitude, the amplifier maintain a constant phase shift. In another scheme (Hornig method),¹¹ data are carried in the form of the amplitude of pulses. The amplifier must have good bandpass so as not to distort the pulses and, of course, must be quite linear in amplitude.

Electronic circuits are used in many pieces of auxiliary gear for spectrometers and only a few will be mentioned here. One example of such equipment is the electronic slit drive. In one instrument a tapered potentiometer is driven by the wavelength shaft. As the wavelength changes, a servo positions the slits according to data received from this potentiometer. The taper is chosen so that the slit adjustment removes the energy variation which would result from the black body characteristics of the source. Thus, reasonably constant energy is passed through the monochromator regardless of wavelength setting. In another system^{10, 11} a signal is available which is proportional to reference I_0 signal. In this case the servo system can be used to adjust the slits so that I_0 remains constant.

Photometry System. The term "photometry" is used to apply to the principle of radiation measurement. The instrument in Figure 1 uses single-beam photometry: the radiation from source without sample and with sample are measured separately, a

ratio calculated and replotted. Complete spectral plotting by such a method is tedious and rarely done. Such replotting is not particularly necessary for internal spectral use but is desirable for external dissemination on some absolute scale.

In order to avoid this difficulty, instruments have been developed which provide automatic comparison of the intensity of the reference (I_0) beam and the sample (I) beam. Such instruments are termed "infrared spectrophotometers." These approaches to this automatic comparison have been described—the memory method,¹² the optical null,⁷⁻⁹ and the direct ratio.^{10, 11}

In the memory method a single beam photometer is used. The I_0 spectrum is recorded and a slit servo operated to maintain the I_0 value constant. The slit schedule required is recorded on tape or wire. The sample is introduced, and the spectrum rerun with the slits repeating the schedule on the tape.

In the optical null method, two radiation beams are taken from the source and, by means of a rotating mirror, each beam traverses the monochromator detector system on alternating half cycles. If the two beams have the same intensity, they will produce a d.c. signal at the detector. If they are unbalanced, an a.c. signal results. The sample is placed in one beam and a diaphragm device graduated from 0 to 100% transmission in the other. The a.c. signal resultant from unbalance is used to drive the diaphragm to balance and at its balance position it records the transmittance of the sample. A schematic of such a system is shown in Figure 2.

The direct ratio system is similar to the optical null in that two radiation beams are simultaneously compared. In this case a separate electrical signal proportional to each beam is separated by a phase sensitive detection system. The I_0 signal is placed across the slide wire of a recording potentiometer and the I signal fed to the con-

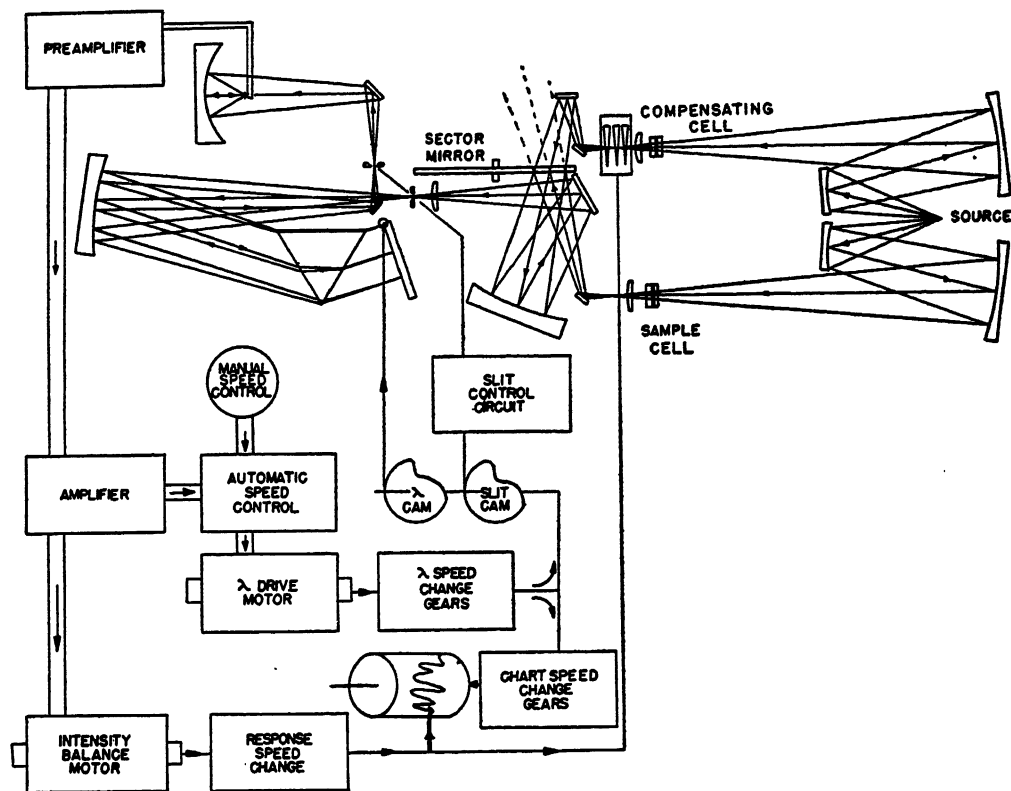


FIG. 2. Schematic diagram of optical null-type infrared spectrophotometer.

ventional recording point so that the ratio I/I_0 is automatically attained.

There are advantages and disadvantages to all the schemes both inherently and because of other experimental limitations. These points are discussed in references 13, 14 and 7. In the course of time, one of these systems or a combination may prove predominant.

Recording Variables. The various instrument elements discussed above are combined in operation to provide an infrared absorption spectrum. The quality of the spectrum, and therefore the quality of the instrument, can be judged by four fundamental operating variables: (1) spectral resolution, (2) reproducibility, (3) time of recording, (4) accuracy. These are not independent variables as it is not possible with a given instrument to set arbitrary

values for each variable. Therefore, a spectrum cannot always be judged as to any one variable without regard to the others.

Spectral resolution defines the degree to which sharp, adjacent absorption bands can be resolved or shown as separate bands. It is primarily a function of the spectral slit width used, but it is also dependent on the response of the recording system at the scan speed and the reproducibility conditions. Optical resolution by itself can be measured by spectral tests under slow low noise recording. A spectrum may show a lack of resolution because it is recorded at too high a speed for the recording system to follow the spectral structure. For a given instrument, the spectral slit width determines the radiation or electrical *signal* available for measurement. For prism instruments, spectra are usually recorded with a spectral

resolution of 2-4 times the Rayleigh limit term of Equation (2).

Reproducibility defines the degree to which two spectra, taken under identical instrument conditions, can be superimposed. It depends on the mechanical and electrical reproducibility of the equipment and the theoretical electrical Johnson noise. Assuming adequate design performance, the ultimate limit is then the theoretical noise limit. It is usually measured by running a 3-5 minute record under operating conditions, but with the radiation source shuttered. Two parallel lines are drawn to just enclose this record and the separation of the lines is the peak-to-peak noise. RMS noise is about one-fourth this value. This figure, expressed in equivalent radiation or electrical signal limits, provides the basis for a ratio of *signal-to-noise* used in recording the spectrum. Normal signal-to-noise ratios used are from 50-300. Johnson noise is varied by the filter band-pass control.

Time of recording is simply the elapsed time required to obtain the spectrum shown. Generally, in running a spectrum, the instrument is set for the desired spectral resolution which then determines the signal. The required signal-to-noise ratio is then determined by adjusting the bandpass which fixes the noise. Such a bandpass setting also fixes the response time of the instrument, a measure of the time required for the recording pen to react to a sharp change in signal. With these variables determined, sufficient recording time must be allowed for the system to measure the spectral structure. Spectral recording time for the NaCl region 4000 cm^{-1} ($2.5\text{ }\mu$) to 650 cm^{-1} ($15\text{ }\mu$) runs from 5 to 45 minutes.

Accuracy, the fourth variable, has two connotations. The obvious one is a measure of the deviation of abscissa designation from true frequency (wavelength) or ordinate designation from true transmittance of a sample. The abscissa accuracy is primarily a

design function, while ordinate accuracy is a function of sampling, false radiation, and design features of the photometry system chosen. Abscissa variation is usually $\frac{1}{2}$ -1 part in 1,000 and ordinate accuracy $\frac{1}{4}$ -1 part in 100. Ordinate accuracy is often dependent on sampling and operator techniques.

The above accuracy discussion holds for static measurement or measurement at very slow recording speed. Under these conditions, accuracy is subject to design or operator control. As recording speed is increased, the noise requirement and consequent band-pass set a theoretical limit on the degree to which structure can be followed accurately. Such deviations have not been given much consideration since, for most of the applications of infrared, reproducibility rather than true accuracy is the prime requisite.

The Continuous Analyzer (Process Analysis)

The instruments discussed above are used primarily for research or control laboratory applications on batch sampling. There is an increasing extension of infrared instruments to plant process continuous analysis and control. The basis and usefulness of such equipment are the same as that previously discussed, the main difference in the two types is that in the process equipment elasticity of use has been sacrificed for extreme stability and dependability. The instruments are of two types—dispersion and non-dispersion.

The dispersion instruments follow the types already outlined. Dimensions, and sometimes optical quality, are reduced for economy; ease of slit and wavelength adjustment are sacrificed for permanence. Thermostating and explosion proofing are common practice. As in the laboratory instruments a comparison of two signals is desired to remove the effect of source variations and give results on an absolute basis. In one process instrument, the bichromator analyzer, a

single sample cell is used but two radiation wavelength bands, λ_1 and λ_2 , both passing through the sample, are compared automatically and continuously. A second pilot plant-type instrument¹⁴ makes successive comparative measurements at six pairs of wavelength positions, the first of each pair being used to standardize the instrument and the second for the component absorption.

In the non-dispersion instrument, prisms or gratings are not used. Instead, total radiation from a source is passed through a sample and variations in the radiation are correlated with change in sample concentrations. Such instruments fall into two general categories based on the use of selective^{17, 18} or non-selective^{15, 16} radiation detection. At first thought the non-dispersion type of instrument would seem to have less component selectivity than a dispersion type one, i.e., would have less possibility of measuring a component of a mixture uniquely because the use of absorption bands over the whole spectral range would imply more spectral overlap with the other components. Although there is a much greater probability of overlap, this has been turned to advantage in a method of "compensation"¹⁹ whereby, in many cases, the non-dispersion analyzer can be made more nearly unique than a dispersion type. Such continuous analyzers at the present time generally measure only a single component although development of multicomponent types will continue.

REFERENCES

1. RUPERT, C. S. AND STRONG, J. *J. Opt. Soc. Am.*, **40**, 455 (1950).
2. Perkin-Elmer Instrument News, II, No. 2, 4 (1951).
3. HORNIG, D. F. AND O'KEEFE, B. J., *Rev. Sci. Inst.*, **18**, 479 (1947).
4. BILLINGS, B. H., HYDE, W. L., AND BARR, E. E., *J. Opt. Soc. Am.*, **37**, 123 (1947).
5. GOLAY, M. J. E., *Rev. Sci. Inst.*, **18**, 357 (1947).
6. SIMPSON, O. AND SUTHERLAND, G. B. B. M., *Science*, **115**, 1 (1952).

7. WHITE, J. U. AND LISTON, M. D., *J. Opt. Soc. Am.*, **29-41**, 93-101 (1950).
8. BAIRD, W. S., O'BRYAN, H. M., OGDEN, G., AND LEE, D., *J. Opt. Soc. Am.*, **37**, 754 (1947).
9. WRIGHT, N. AND HERSHEY, L. W., *J. Opt. Soc. Am.*, **37**, 211 (1947).
10. SAVITZKY, A. AND HALFORD, R. S., *Rev. Sci. Inst.*, **21**, 203 (1950).
11. HORNIG, D. F., HYDE, G. E., AND ALCOCK, W. A., *J. Opt. Soc. Am.*, **40**, 497 (1950).
12. HAWES, R. C., *et al.*, Symposium on Molecular Structure and Spectroscopy, Ohio State Univ., June, 1949.
13. HAWES, R. C. AND GALLAWAY, W. S., *Science*, **113**, 54 (1951).
14. WHITE, J. U., LISTON, M. D., AND SIMARD, R. G., *Anal. Chem.*, **21**, 1156 (1949).
15. WRIGHT, N. AND HERSHEY, L. W., *J. Opt. Soc. Am.*, **36**, 195 (1946).
16. PFUND, A. H. AND FASTIE, W., *J. Opt. Soc. Am.*, **37**, 762 (1947).
17. WATERS, J. L., AND HARTZ, N. W., presented before Instrument Society of America, Houston, September, 1951.
18. LUFT, K. F., *Z. Tech. Physik*, **24**, 97 (1943).
19. KOPPIUS, O. G., *Anal. Chem.*, **23**, 554 (1951).

PERKIN-ELMER CORPORATION

INTERPRETATION AND CATALOGING

An infrared absorption spectrum of a sample is generally obtained for one of four major reasons. The sample may be an unknown compound for qualitative identification, a mixture of known components for quantitative analysis, a newly synthesized compound whose structure is to be elucidated, or a compound on which data are desired concerning the physics of the molecule such as force fields inside the molecule or vibrational contributions to specific heats. The procedure for making use of, or interpreting the spectral data varies with the type of information desired.

Quantitative analysis is the mathematical resolution of the spectrum of a mixture of compounds into the percentage of each compound which must be present to give the resultant total absorption. Procedures for quantitative analysis are discussed in detail elsewhere.

In *qualitative analysis* an unknown compound is identified by point-by-point spectral matching with a previously established standard. After a spectrum of an unknown compound is obtained, the analyst is faced with a data retrieval problem since the right spectrum for comparison must be located. Some ways in which qualitative analysis is achieved are discussed below.

The simplest qualitative analysis problem is the one in which the unknown is submitted for analysis along with a reference sample of material which it is expected to match. Spectra of the unknown and the standard can be obtained under identical instrument conditions and comparison of the spectra is a simple procedure. If an exact spectral match is obtained, the analysis is completed. If the spectra are different, then the spectroscopist calls upon functional group data presented to him by the spectrum to obtain a lead on the kind of compound it may be.

These structural group data are empirical information accumulated from the study of spectra of known compounds. Specific atomic groups absorb within a given wavelength region which can be used to characterize that group. The precise frequency at which the group will absorb within this expected region is dependent upon molecular environment factors such as the mass or electronic characteristics of neighboring groups; this information is steadily being accumulated and is reported in the literature. The most comprehensive treatment available is the book "The Infrared Spectra of Complex Molecules" by L. J. Bellamy. A chart of the known correlations is given in the *J. Opt. Soc. Am.*, Vol. 40, 397 (1950). The spectroscopist uses this information tempered by his knowledge of possible exceptions to establish the type of compound the unknown may be. The next step in the analysis depends upon the method of access to reference files that

the spectroscopist uses. Typical examples are:

Compound Class File. Reference spectra are organized according to structural data which can be deduced from the spectrum. For example, aliphatic carboxylic acids may be in one group, aromatic carboxylic acids in another and aliphatic hydroxy acids in still another category. The spectroscopist uses structural group interpretation of the spectrum to establish the category the unknown falls in and then looks through the spectra of the corresponding compounds for (a) an exact spectral match which identifies the compound, or (b) spectrum details which match those of some particular structure variation within the category and which narrow the possible alternatives down to a few compounds. This system offers excellent possibilities for identifying unknowns and for suggesting possible answers if the exact compound desired is not in the file; it provides a good way for new workers in the field to study spectra of compound classes. Its principal disadvantages are that it requires considerable file maintenance time and does not lend itself readily to dual use as a numerical file. An optimum arrangement is to have two sets of reference spectra available so that a master file can be kept in numerical sequence and a duplicate set can be arranged according to compound classes or according to company research projects on which they are needed.

Punched Cards for Electronic Sorting. A punched card can be made for each compound to carry coded information on position and relative strengths of the absorption bands. Some laboratories use a system of their own (*Anal. Chemistry*, Vol. 25, No. 10, pp. 1457-1460, 1953). Others use a system developed by L. Kuentzel at Wyandotte Chemical Company and adopted by ASTM Committee E-13 for standardization and distribution through ASTM Headquarters at 1916 Race Street, Philadelphia, Pennsylvania. An important aspect of this set of

IBM cards is that all of the available reference spectra, including curves from the technical literature are included. If this system is to be relied upon for identification of unknowns by mechanical sorting, it is desirable to have a sorter close to the spectrum files. Most users of these IBM cards find it expedient to break them down into presorted decks so that the entire group of about 15,000 will not have to be processed for a single unknown.

Needlesort Cards. Two of the reference spectrum libraries—the National Bureau of Standards-National Research Council publication and the "Documentation of Molecular Spectroscopy" by Butterworth's Scientific Publications—are available printed on cards punched for needle-sorting on the basis of absorption bands, physical constants and structural groups. It is important for convenient handling of these sets to keep the spectral cards in a presorted system.

Numerical File of Spectra with Access Provided by Indexes. An empirical formula index and alphabetical index can be used to search out compounds known to be possibilities from sample history, physical constants and structural group interpretation of the infrared spectrum. If a "good guess" is available from either a distinctive spectrum or from known possibilities of the sample origin, this system is entirely satisfactory. On the other hand it is apt to fail completely or be unduly time-consuming for many unknowns.

Index by Major Absorption Bands. An index system based on major absorption bands has given good service in many laboratories. It is essentially a notebook file listing all the compounds which have a strongest band at some frequency. It may be broken down into sub-groups by other bands. A commercially available system based on this philosophy of indexing by major bands in each one micron interval is the Spec-Finder by the Sadtler Research Laboratories in Philadelphia. This system is in effect a

card-file which is already presorted by major bands and printed in notebook form. It lacks the flexibility of an indexed card-file, but has the advantage of providing a quick answer (on the order of a few minutes) on many unknowns.

The greatest limiting factor for all the systems is that not enough high-quality reference spectra are available. A laboratory doing diversified analyses needs all of the spectra it is possible to obtain.

Structural Elucidation of an Unknown Compound

Structural group data referred to in the above section are the most useful information for interpretation of the spectrum of a compound for which previous reference spectra are not available. If it is a chemical prepared within the research organization, it is generally very useful to study spectra of the intermediates and see if the spectrum is consistent with the step-by-step chemical modifications. Spectra of closely related model compounds will generally be needed for the spectroscopist to gain confidence in the exact identity of the compound. Absolute proof of the identity of a new compound usually rests upon supporting spectroscopic data such as Raman, on nuclear magnetic resonance, and on chemical evidence.

Theoretical significance of infrared absorption spectra is discussed in "Molecular Vibrations" by Wilson, Cross and Decius (McGraw-Hill) and "Infrared and Raman Spectra" by Herzberg (Van Nostrand).

REFERENCES

- BELLAMY, L. J., "Infrared Spectra of Complex Molecules," Wiley, 1954.
- CRAWFORD, B. L., "Chemical Analysis by Infrared." *Sci. Am.*, **189**, 42 (1953).
- HARRISON, LORD, AND LOOFBURROW, "Practical Spectroscopy," Prentice-Hall, 1938.
- GORE, R. C., "Infrared Spectroscopy—Analytical Reviews," *Analytical Chemistry*, Vol. 30, No. 4, 1958; Vol. 28, No. 4, 1956; Vol. 26, No. 4, 1954.
- HERZBERG, G., "Infrared and Raman Spectra of Polyatomic Molecule," van Nostrand, 1945.

INFRARED SPECTROPHOTOMETRY

JONES, N., AND SANDORFY, C., *Chem. Appl. of Spectroscopy*, "The Application of IR and Raman Spectrometry to the Elucidation of Molecular Structure," Vol. 9 of Weissberger's "Techniques of Organic Chem.," Chapter IV. Interscience, 1956.

LORD, R., McDONALD AND MILLER F., "Notes on the Practice of IR Spectroscopy," *J. Opt. Soc. Am.*, **42**, 149 (1955).

WILSON, CROSS AND DECUS, J. C., "Molecular Vibrations," McGraw-Hill, 1955.

CLARA D. SMITH

LABORATORY ORGANIZATION AND OPERATION

This subject must be considered in relation to the particular type of work to be done and to other available analytical and research facilities. Molecular spectroscopy is applied to the determination of individual compounds and specific structural groups, or to the determination of energies associated with electronic, vibrational, or rotational motions of the molecule. It is in the first area, where a laboratory is offering services, that attention to systematic organization is important. The major types of services offered by a spectroscopy laboratory are:

- Routine control analyses

- Analytical services including quantitative and qualitative analyses

- Research in new applications and analytical method procedure

- Research in instrumental methods and physical measurements of optical and electrical properties of materials for sources, detectors, and windows

Most laboratories will function at one time or another in more than one of these areas. For purposes of describing essential equipment, personnel, administration, and auxiliary services it is useful to consider them separately.

The routine control laboratory may range from a single spectrometer suited to one determination for a fabricating company with a minimum need for chemical work, to a large array of spectrometers for routine

monitoring of many phases of production of chemicals. Where several instruments are applied, and where there may be a frequent change in the specific analyses needed, the subsequent discussions on general analytical and research facilities are likely to be more applicable than this particular section.

Consider as typical of the simplest type of spectroscopic installation the requirements of a company manufacturing refrigerators for an analysis for water in "Freon," or of a company using organic solvents in a formulation as a means of checking ratios of components in the solvent from the supplier. Such instrumentation needs may best be served by equipment which is ruggedly built for minimum damage by the atmosphere and idly probing fingers. A single table with storage drawers may serve as the entire laboratory unit. Desirable features for other spectroscopy laboratories such as direct-recording attachments and air-conditioning are not essential here.

Careful operators or technicians can perform routine analyses after instruction from a spectroscopist who may be available from the instrument manufacturer or from consulting firms. Such instruction should culminate in a step-by-step written procedure which is explicit in every detail and which includes symptoms for recognition of faulty instrument performance. Details which should be covered are: sampling procedure and sample manipulation, with emphasis on most likely sources of error; cell blank and, in the case of infrared, cell thickness determination; instrument response and background energy characteristics; instrument settings for making the determination; procedure for measuring peak intensity and for the mathematical or graphical conversion of this intensity to the desired analytical results. One of the most useful and trustworthy over-all checks is the analysis of a standard with every sample or at several intervals throughout the day.

In most cases auxiliary equipment would

include sample cells and dry storage units for them; hypodermic syringes for convenient cell-filling; solvents for cell-cleaning and sample dilution; volumetric glassware and an analytical balance if needed for the specific analyses in question. A laboratory limited to routine control work will need only those reference spectra which pertain to the analysis on hand.

The spectroscopic laboratory which offers analytical services to a research organization will require better trained and more versatile personnel than the control laboratory. There should be a large proportion of college-trained chemists on the staff. It is a truism that each specialized area of spectroscopy should be the direct responsibility of a strong advocate of that field who knows fully the theoretical limitations of its application and acknowledges no other limitations. The conviction that it is possible to obtain a given sensitivity or characterization appears essential for the painstaking attention to detail necessary for development of refined procedures. At the same time, each specialist should be well enough informed about the other available spectrometers and about chemical methods of analysis to avoid doing something the hard way. If the staff members do not have an adequate technical background, university short courses or courses by the instrument manufacturers are helpful.

Management responsibility for an analytical spectroscopic laboratory must include a systematic way of handling repetitive samples and a flexible procedure for keeping the practicing spectroscopists close to the research programs on which their services are to be required. It should encourage research-mindedness on the part of the analyst. Faced with a spectrum, a spectroscopist must ask himself the right questions before he can arrive at correct answers. These questions must arise from his familiarity with the problem to be solved. This need for an understanding by the spectroscopist of the research problem which requires spec-

troscopic data arises at the beginning of the planned research program. If the spectroscopist studies the problem and helps direct the research along lines amenable to solution by his resources, the chances for solution of the problem are optimum.

It may not appear obvious why this advance consultation is important when "all that is needed is an analysis." Consider a new synthesis product which has been submitted for infrared analysis. The submitter wants to know if it is pure. The spectroscopist may confirm from functional groups present that the spectrum is consistent with the anticipated structure. He may note the absence of possible contaminating structures. He may even, if the compound happens to be one with sharp symmetrical peaks with few shoulders and little broad absorption, be able to say that the spectrum gives a fairly "clean" appearance as if the compound were pure. These comments would be the limit of his analysis. If, on the other hand, he is consulted in advance, he will recommend submission for analysis of the starting material and any chemicals used which, from physical properties, might still be expected to be present; he will ask for samples of the product at intermediate steps; and he will want some of the final product at various stages of purification. From these samples he will be able to establish the wavelengths of characteristic absorption of any of the likely impurities and report on their absence in the final purified product. The intermediates or products of side reactions may have functional groups in common with the desired compound and escape detection unless such step-wise spectra are obtained so that "fingerprinting" bands can be used. The chemist must be alerted by the spectroscopist to save samples from the various synthesis steps or this kind of analysis will not be possible.

Basic instruments for a versatile analytical laboratory should, as a minimum, cover ultraviolet and visible, and the sodium

chloride (2 to 15 micron) region of the infrared. Spectrometers designed to cover ultraviolet, visible and the near infrared region (to 3 microns) are available as a single unit and would provide good flexibility. If an infrared prism material other than sodium chloride is desired for some special purpose, it is most practical to have two infrared spectrometers so that service in the sodium chloride region is not disrupted. The second infrared spectrometer can then be used alternately with lithium fluoride or calcium fluoride optics for improved resolution in the higher frequency regions or with potassium bromide or cesium bromide optics for extension of the spectrum to 25 or 35 microns, respectively. For most identification work and quantitative analyses the sodium chloride region is the most valuable, and primary importance should be attached to obtaining good instrumentation there. It is seldom that either the high resolution obtainable from grating spectrometers or the special information available from Raman spectra is needed in the analytical service laboratory.

Instruments for the analytical laboratory should be selected for reliable performance and ease of operation. Automatic recording spectrometers which present the spectrum already compensated for all variables except sample absorption are especially desirable. At the present time this seems to be most simply achieved by double-beam spectrometers. Standard accessories described in literature of spectrometer manufacturers will generally fill analytical requirements.

Routine laboratory preparedness should include:

1. Daily spectrometer performance checks
2. Periodic cell blank determinations
3. Periodic cell thickness determinations for infrared cells
4. Blanks on solvents
5. A spectrum reference file
6. Log books on instrumentation and on samples

7. A file of descriptions of analytical procedures so that repetitive samples are routinely handled

The spectral reference file and cell thickness determinations are special to spectroscopy laboratories and are considered here in detail:

Spectrum Reference File. A good spectrum reference library for a versatile analytical laboratory follows in importance only the personnel and spectrometers. With a good accessible file, the spectroscopist can tell immediately which analyses of mixtures are feasible and what bands should be used. He can predict fairly well the probable accuracy of the analysis with no delay for laboratory work. He can positively identify any of the thousands of compounds for which he has infrared reference spectra and give an order-of-magnitude assessment of purity. He can line up the spectra of compounds with some particular combination of structures that are expected in a new compound and use these spectra as a basis for interpretation of a new synthesis product. The immediate applications that a spectroscopist can make of his equipment are limited to the reference data that he has available. He can, as needed, obtain his own reference spectra but this is a costly, delaying approach compared to having the spectra already on hand.

Reference spectra appear in the technical journals and in far greater numbers in commercially available sets. Briefly, these sets are published by The American Petroleum Institute, Sadtler Research Laboratories, The National Bureau of Standards, Documentation of Molecular Spectra by Butterworth's Scientific Publications and Verlag Chemie and The Coblenz Society Spectrum Collection. Descriptions of all but the latter are summarized in *Applied Spectroscopy*, Vol. 11, No. 2, p. 108.

Data retrieval from the spectrum sets is achieved in various ways: IBM data cards produced by the American Society of Testing Materials furnish a means of machine

sorting all of the spectra in the periodicals as well as the various spectrum catalogs. Each system supplies empirical formula and/or alphabetical lists of the spectra. The Sadtler Laboratories publishes a Spec-Finder which is essentially a notebook index of the spectra according to major absorption bands. The National Bureau of Standards and Documentation of Molecular Spectra sets are available on punched needle-sort cards.

Each of these retrieval techniques is very useful in certain types of applications. A diversified laboratory will probably require more than one system for its many types of problems. A filing system favored by many spectroscopists consists of categories derived from chemical structure and, therefore, spectral characteristics. Such a system groups together closely related spectra and relies on the spectroscopists to recognize the compound class from the spectrum for retrieval of reference data. This is an extraordinarily useful arrangement for the principal compound classes. It becomes unwieldy, or requires multiple copies of spectra for cross-filing for complex molecules with several different functional groups.

There is an important gap in the literature on molecular spectra. For example, infrared spectra of only about 25,000 compounds have been published. This is a small proportion of the more than one million known organic molecules. Even fewer ultraviolet and Raman spectra are published.

Sample Cells. Cells for ultraviolet and visible spectra are usually one centimeter long and are provided constructed accurately by the manufacturer. Infrared absorption cells are commonly made of sodium chloride for use in the 2 to 15 micron region. The thickness of the sample space for liquid samples and solutions is most commonly 0.01–0.50 mm, although it may range from 0.001 mm–5.0 cm for special applications. Cell thickness can be measured from interference fringe patterns obtained by running a spectrum of an empty cell (*Trans. Fara-*

day Soc., **14**, 171 (1945). The thickness is calculated from the following formula:

$$\text{thickness in microns} = \frac{n}{2} \frac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_2)}$$

where n = number of fringes between wavelengths λ_1 and λ_2 .

This determination is applicable only when the cell windows are plane and parallel. Any irregularities in the cell windows which affect the cell thickness will not be taken into account. Too, cells change thickness during use and damaged cells often will not provide interference patterns. The relative thickness of cells used in a laboratory is the critical value from the standpoint of quantitative analysis. A practical means of maintaining a relative calibration of the cells which is more accurate quantitatively than interference determinations is as follows: For all new cells determine thicknesses by interference measurements. Then run a spectrum of some convenient liquid like 2,2,4-trimethylpentane under standardized instrument conditions in each cell. Select bands in the favorable intensity range for accurate quantitative measurements, about 0.2–0.7 optical density, and measure them for all cells. Construct calibration curves of optical density vs. thickness as determined by interference fringes for several bands of different intensities. The strongest bands will be useful for the thinnest cells. These curves can be used to provide precise calibration of quantitatively effective thickness of all future cells just from a measurement of the spectrum of the selected liquid in the cell. This standardized system for maintaining cell thickness data will save many times over the time necessary for establishing the calibration data.

The physical layout of the laboratory should provide enough area for the spectrometers to be accessible from all directions for servicing; stable electrical service; dust-free, constant temperature, low humidity (below 40% RH) atmosphere; sample handling

facilities including hoods for work with solvents, vacuum drying apparatus, gas-handling equipment, press for making pellets; and accessory items commonly needed to provide for reflectance measurements, polarization studies, and micro-samples. In conjunction with, or included in the spectroscopic facilities should be equipment for sample fractionation: chromatography, distillation and extraction.

The spectroscopic research laboratory will require the same facilities, generally, as the diversified analytical laboratory. In addition, flexible spectrometers which adapt readily to changes in optical path, sources and detectors are valuable. The research personnel require backgrounds in chemistry and physics with special emphasis on molecular structure, organic reactions, analytical chemistry, micro and gas techniques and electronics.

Special information provided by nuclear magnetic resonance, para-magnetic resonance and Raman spectroscopy should be considered as possible inclusions for the large spectroscopic research laboratory.

CLARA D. SMITH

LONG-CHAIN FATTY ACIDS

Fatty acids are substances with the general structural formula $\text{CH}_3(\text{CH}_2)_n\text{COOH}$, in which n is any integer from one to infinity. Biologically important, these monocarboxylic acids occur naturally as esters of mono- or polyhydric alcohols, especially of glycerin (tri-esters of which are called fats). Butyric acid, $\text{CH}_3(\text{CH}_2)_2\text{COOH}$, and stearic acid, $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$, are two of the most common normal aliphatic acids.

Almost without exception, natural fatty acids occur in mixtures with homologs, usually those in which the chain differs by two or four methylene groups. Because the methylene chain is relatively inert, homologous fatty acids differ but little from each other in chemical and physical properties, and they are difficult to separate and to

prove pure. Almost any measurable property of a single fatty acid can be closely matched by one or more appropriate mixtures of homologs. Infrared spectroscopy can offer the least ambiguous identification of an unknown fatty acid, but the special properties of this family of compounds must be taken into consideration.

Fatty acid molecules exist in the liquid and solid states almost exclusively as dimers with pairs of molecules held together by mutual hydrogen bonding of their carboxyl groups. In the crystal, the zig zag methylene chain is constrained to lie in a single plane. However, in the molten state or in solution the chain may twist about one or more C—C bonds, so that each fatty acid molecule is likely to wriggle into a conformation somewhat different from those of its neighbors. Infrared and X-ray studies reveal that on heating a fatty acid crystal to within a few degrees below its melting point, some conformational isomerism occurs. After melting, virtually no chains remain planar. In an orderly crystal, certain sharp infrared bands appear which are characteristic of the individual fatty acid. These bands happen also to be sensitive to the shape of the chain. In a molten sample, these sharp bands are replaced by broad contours, indicating that the distribution of chain shapes is relatively independent of chain length.

About a dozen infrared bands characterize a specimen as a member of the fatty acid family. These group vibrations are produced by simple functional groups with little influence from the rest of the molecule. They are listed as follows:

3500-3000 cm^{-1}	O—H stretching (broadness shows strong hydrogen bonding)
2954	C—H asymmetrical stretching of CH_2
2926	C—H asymmetrical stretching of CH_3
2872	C—H symmetrical stretching of CH_2

2853	C—H symmetrical stretching of CH ₂
1710	C=O stretching
1460	CH ₂ bending
1410	CH ₂ bending of methylene adjacent to COOH
1372	CH ₂ symmetrical bending
1300	C—O stretching coupled with O—H in plane bending
940	O—H bending out-of-plane
720	CH ₂ rocking of four or more consecutive methylenes

In solution or molten sample, most fatty acids have virtually the same spectrum, for the above-mentioned bands are the only well-defined ones. This anonymity of homologs is a characteristic peculiar to long-chain compounds. In the spectra of most other compounds, "fingerprint" bands are present which are sensitive to nuances of molecular structure and confer uniqueness upon each infrared spectrum. However, most other compounds have their functional groups close enough to influence each other, and their molecular geometries remain relatively constant in transitions between physical states. Long-chain compounds, on the other hand, undergo great changes in shape in the random environment of a liquid, and the functional groups at the chain ends have little influence on each other because of the large separation.

In contrast to the paucity of detail shown in the spectra of liquefied fatty acids, the same compounds when crystalline present additional sharp "fingerprint" bands which can distinguish homologs. However, these infrared-active vibrations are so sensitive to physical state that they vary in intensity and frequency with slight changes in crystal structure.

Fatty acids frequently possess more than one crystal form, a property which is called *polymorphism*. The infrared spectrum of each form is distinctive, so that superimposition of the spectra of unknown and known specimens demonstrates identity not only of the molecules but also of the crystal

lattice. Sometimes the spectra differ in slight detail because of failure to achieve well-defined crystal forms, or because of crystal orientation effects; but ordinarily specimens carefully prepared in the same way will yield identical spectra. Should discrepancies arise, several correlation methods which are to be described below may be helpful.

The additional bands possessed by crystalline fatty acids are relatively weak, and fall into two main categories: (1) the C—C—C skeletal modes which cover the broad range from 725–1150 cm⁻¹ and differ from each other greatly in intensity, and (2) the CH₂ wagging modes, restricted to the range 1180–1360 cm⁻¹, which tend to be rather uniform in spacing and intensity. The latter group of bands is common to long-chain aliphatic compounds, and each set of bands is called a band progression. In both 1 and 2, it is the coupling of many identical units vibrating in the same mode that tends to create just as many bands differing from each other periodically in frequency. This coupling is sensitive to CH₂ chain length, the end groups, and steric effects.

The task of distinguishing homologous fatty acids other than by spectral superimposition is essentially one of determining the length of the methylene chain. One method is based on the fact that the molar absorption intensity of the 2850 cm⁻¹ band (C—H stretch of CH₂ group) is directly proportional to the number of CH₂ units in the molecule. This method requires precise measurement to distinguish the C₁₇ from the C₁₈ fatty acid and is best done on solutions. To avoid the task of quantitative preparation of the solution, the intensity of the 2872 cm⁻¹ band of the single CH₃ group may be used as an internal standard. A false result may be obtained because a mixture of homologs may yield an average chain length corresponding to none of the actual components. Also, an impure sample may seem to be the wrong homolog. This method of identification

therefore has little to offer except perhaps to supplement other data.

Two other methods, the Average Spacing method and the Rule of Two are available for identifying fatty acids, and both utilize the band progressions. For the fatty acids, these bands are limited to the 1178–1360 cm^{-1} range, and the number of bands in each progression increases with the number of methylene groups. Theoretically, one band should exist for each CH_2 , and the spacing between bands should vary. In reality, the full number of bands exists, but they are arranged in pairs of irregularly but closely spaced bands which apparently merge into single bands that are uniformly separated. The more bands in the progression, the smaller the average spacing between bands. The Average Spacing method therefore relates the average band interval to the chain length, and the Rule of Two counts the number of bands within a specified frequency limit.

In the Rule of Two method, the progression bands between 1178 and 1347 cm^{-1} are counted, and the total number of carbons in the chain is twice the number of bands. The 1347 cm^{-1} limit is arbitrary, for progression bands are actually observed up to 1360 cm^{-1} , but the simplicity of the rule permits tentative identification of fatty acids until reference spectra can be obtained. Odd chain length fatty acids have the same number of progression bands as the next lower homolog except that for the odd chain all the progression bands are shifted to slightly lower frequencies. The stronger, broader 1300 cm^{-1} band produced by the $-\text{COOH}$ group sometimes makes the progression bands less apparent, particularly when the specimen is poorly crystallized, and then the simple Rule of Two is difficult to apply.

The Average Spacing method, in which the fairly uniform intervals between adjacent bands are measured and the average calculated, gives a number sufficiently different for each homolog to distinguish it from

the others. Furthermore, it is not necessary to resolve the complete set of progression bands although the more that are measured the more precise the calculated average spacing becomes. Odd chain lengths fit right on the curve relating spacing and chain length. A table of experimentally found average spacings is given below.

Fatty Acid Chain Length	Frequency Difference in cm^{-1}
C_{10}	34
C_{12}	28
C_{13}	26
C_{14}	24
C_{15}	22
C_{16}	20.4
C_{17}	19.5
C_{18}	18.0
C_{19}	17.3
C_{20}	16.0
C_{22}	14.6
C_{24}	13.5
C_{26}	12.8
C_{28}	11.1
C_{30}	10.7
C_{36}	9.2

Interpolation can be used to identify intermediate homologs.

Fatty acid specimens need not be especially pure in order to present sharp progression bands. In fact, a 1:1 solid solution of two fatty acids yields a jumble of bands that are seen to be the two overlapping band progressions. This is surprising, considering that mixed dimers are present along with matched dimers. That the carboxyl group effectively shields the chain from the moiety on the opposite side is brought out by the identical band progressions found in the various alkyl stearates. Planarity of the chain is perhaps the most important factor in obtaining sharp, consistent band progressions, and so the sample must be well crystallized. In this respect, the Nujol mull technique is quite satisfactory and most convenient. In solid film preparations, crystalline orientation may alter band intensities somewhat, and too rapid cooling may give rise to mixed crystalline forms. The KBr

pellet technique yields the sharpest spectra, the pressing having no apparent effect on crystal form, although the heat resulting from too vigorous mixing should be avoided.

The superimposition of well-defined infra-red spectra of crystals affords the best means of identification of a fatty acid, but many workers will not have ready access to a comprehensive library of spectra. In this case, the application of one or more of the above-described correlations to the examination of the unknown spectrum can provide a tentative identification which will simplify the task of finding the matching reference spectrum. The quantitative comparison of absorption intensities of bands due to methylene and methyl groups has the advantage of not requiring a crystalline specimen, but this method is not very useful because it may yield a false result for an impure sample. This risk is minimized with the other two methods, but they require carefully crystallized specimens. Of these the Rule of Two is slightly easier to apply, but it is hard to distinguish between an even-chain fatty acid and its next longer odd-chain homolog. The Average Spacing correlation is the most useful of the three, for the measurement is simple, and the graph of the spacings for both odd and even fatty acids versus chain lengths yields a single smooth curve.

REFERENCES

1. ARONOVIC, S. M., Ph.D. Thesis, Univ. of Wisconsin, 1957; *Dissert. Abs.*, 17, 743 (1957).
2. GORE, R. C., AND WRIGHT, E. S., in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, ed., p. 219, New York, Academic Press, Inc., 1955.
3. JONES, R. N., MCKAY, A. F., AND SINCLAIR, R. G., *J.A.C.S.*, 74, 2575 (1952).
4. MEIKLEJOHN, R. A., MEYER, R. J., ARONOVIC, S. M., SCHUETTE, H. A., AND MELOCHE, V. W., *Anal. Chem.*, 29, 329 (1957).
5. O'CONNOR, R. T., FIELD, E. T., AND SINGLETON, W. S., *J. Am. Oil Chem. Soc.*, 28, 154 (1951).

6. SINCLAIR, R. G., MCKAY, A. F., AND JONES, R. N., *J.A.C.S.*, 74, 2570 (1952).

7. VON SYDOW, E., *Acta Chem. Scand.*, 9, 1119 (1955).

SANFORD M. ARONOVIC

LONG-PATH SPECTROPHOTOMETRY

The spectral region of particular interest (1-15 microns) which is associated with molecular vibrational and rotational motions of atomic and molecular sub-groups of the total molecule has been used in chemical analyses for measuring the presence and concentration of gases and vapors in trace amounts [parts per million by vol. (ppm)].

The key component of a spectrophotometer for long-path studies is a multireflection absorption cell. The design initiated by John U. White in 1942 has served as the foundation for the most significant developments in this field for laboratory type research and analysis. However, important work has been carried out with direct long-paths in tubes or pipes as well as in the open atmosphere.

The basic scheme of the cell involves three spherical mirrors all of equal radii of curvature. Two are large mirrors (~12 inch diameter) which are mounted at one end of the cell with their centers of curvature on the surface of a smaller spherical mirror mounted at the other end of the cell. The center curvature of this small mirror is between the two large mirrors and in the plane of their surfaces. An external spherical mirror forms an image of the radiation source just off the edge of the small mirror. The beam then diverges to fill the first of the two large mirrors. This mirror forms an image, on the surface of the small mirror, symmetrically placed about the center of curvature of this large mirror. The small mirror in turn reflects the beam to fill the second large mirror. This mirror forms an image of the source just off the edge of the small mirror so that the beam exits from the cell. By decreasing the separation between the centers of curvature of the two large mirrors any integral of four

INFRARED SPECTROPHOTOMETRY

TABLE 1. CONCENTRATIONS AND WAVELENGTHS AT WHICH VARIOUS GASES AND VAPORS MAY BE MEASURED BY AVAILABLE SPECTROMETER SYSTEMS.

Compound	Wavelength at which Compound is Measured (μ)	Lower Practical Measuring Limit (ppm)
nitrous oxide	4.50	0.20
nitric oxide	5.25	0.50
nitrogen dioxide	6.15	0.15
n-butyl nitrite	12.72	0.05
ethyl nitrite	10.78	0.25
	12.80	0.05
acetyl nitrate	8.64	0.02
	12.56	0.02
ethyl nitrate	11.75	0.02
ketene	4.65	0.25
carbon dioxide	2.80	10.0
	4.37	5.0
	13.95	10.0
carbon monoxide	4.62	0.15
ozone	9.52	0.10
propylene oxide	12.00	0.30
formaldehyde	3.60	0.25
water	6.65	100.0
acetone	8.25	0.10
acetaldehyde	5.62	0.20
propionaldehyde	5.62	0.20
methyl alcohol	9.72	0.15
methyl ethyl ketone	8.56	0.15
ethyl alcohol	9.40	0.15
ethylene oxide	11.51	0.30
acrolein	5.85	0.20
	10.50	0.30
trichloroethylene	10.62	0.05
	11.81	0.05
tetrachloroethylene	10.98	0.03
	12.85	0.03
xylene	13.05	0.30
cyclohexane	3.42	0.05
methane	7.68	0.25
isooctane	3.38	0.10
3-methyl pentane	3.41	0.15
n-pentane	3.41	0.15
acetylene	13.74	0.05
ethylene	10.57	0.15
isobutene	11.28	0.10
butene-1	3.40	0.30
	11.00	0.30
2-ethyl butene-1	11.22	0.25
trans-2-butene	10.42	0.20
2,3-dimethyl 2-butene	3.44	0.15
propylene	11.00	0.15
1,3-butadiene	11.04	0.20
diisobutylene	11.20	0.15
cyclohexene	3.42	0.15
isoprene	11.08	0.10
2,3-dimethyl-1,3-butadiene	11.22	0.05
1,5-hexadiene	10.98	0.10
2-methyl trans 2-butene	3.45	0.25
	12.50	0.50
3-heptene	3.40	0.15
cyclooctadiene	3.32	0.25
	3.47	0.25
1,3-pentadiene	11.08	0.20

passes can be obtained. If the base path length is X meters (i.e., the radius of curvature of the mirrors is X meters) and one obtains n passes the total path length is nX . In this manner path lengths up to 800 meters have been achieved with this type of cell.

Experience with these cells has shown that atmospheric water vapor and carbon dioxide do not prohibit useful atmospheric analysis although they do make some regions of the infrared spectrum unusable and present difficulties in others.

The spectrum as it appears with several hundred meters of air of normal humidity is as follows: Absorption is total in the carbon dioxide and water bands at about 2.9 microns but the air is sufficiently transparent at 3.4 microns so that weak CH absorption can be detected. This is especially true if a calcium fluoride prism is used. The region from 3.4 to about 3.9 microns, where characteristic aldehyde absorptions appear, is completely free of water and carbon dioxide absorptions. Absorption is total in the 4.3 micron band of carbon dioxide but the atmosphere is sufficiently transparent to reveal the carbon monoxide band at 4.66 microns. The absorption of naturally occurring nitrous oxide at 4.5 microns cannot be seen unless some of the atmospheric carbon dioxide is removed. The carbonyl region is opaque at hundreds of meters path-length but some energy is detectable in the center of the 6 micron water band. Between about 7.2 and 8 microns usable energy is transmitted although the water band is still strong. Between 8 and 9 microns the water band is troublesome, but not a serious interference. The region 9 to 12 microns, where ozone, methanol, formic acid, and many other absorbers have their strongest bands, is nearly free of interfering absorptions. Beyond 12 microns the water and carbon dioxide bands gradually increase in strength. The strong and characteristic acetylene band at 13.7 microns is about the last useful band detectable. The 15 micron carbon dioxide

band makes the air opaque beyond about 14 microns.

The use of double-beam spectrometers, which makes possible dual multireflection long path cell operation, has reduced the interferences from CO_2 and H_2O and thus additional wavelengths for analytical purposes are made available. Furthermore, the use of scale expansion has increased the sensitivity of this system so that many gases and vapor concentrations in the ppm range can be measured.

The infrared absorption spectrum of the earth's atmosphere, using the sun as the light source, revealed the presence in trace amounts of methane (CH_4) at 3.3μ , nitrous oxide (N_2O) 7.8μ , and carbon monoxide (CO) at 4.67μ , deuterium hydroxide (HDO) at 3.67μ and ozone at 9.6μ . Horizontal paths up to 5000 yards with man-made radiation sources have been used not only to detect these gases in the lower atmosphere, but also to study the detailed nature of absorption bands of carbon dioxide (CO_2) and water (H_2O).

It is now possible with commercially available spectrometer systems to measure concentrations of gases and vapors as shown in Table 1.

N. A. RENZETTI

MICROGAS CELL

In the analysis of liquid samples by gas chromatography, it is often difficult to identify the different fractions as they emerge from the column. Numerous means have been used, such as collecting the cuts and measuring their absorption spectra, sampling the effluent continuously with an ultraviolet or a mass spectrometer, or making chemical tests on collected cuts. Unfortunately, most infrared spectra are too weak to be measured directly as they emerge from the column. Two ml of gas charged to a column just gives a strong enough infrared spectrum in a standard 10 cm gas cell if

it is a single component. To measure the spectra of minor components, the ratio of path length to cell volume must be increased in proportion to dilution of the components.

A multiple traversal absorption cell has been built for this purpose, using a combination of White's¹ mirror system with the three lens beam condenser described recently by the authors.² Its 100 cm path in 22 ml of volume gives it a ratio of length to volume of 4.5 cm per ml, an increase of 50 to 100 times that of most standard 10 cm infrared absorption cells.

The optical arrangement of the system is shown in Figure 1 as it is used in the Beckman IR-5 and IR-4 spectrophotometers. It may also be fitted in the IR-6 spectrometer by reversing it end for end. The two lenses on the left, L1 and L2, form a five-times reduced image of the slit image, S. It is reflected into the cell through the window, W, by the first surface of the prism, P. After leaving the cell, the image of the slit is reflected back into its original path by the second surface of the prism and remagnified to its original size by the third lens, L3. The beam condenser has been modified from the one that was described previously to increase the free space around the reduced image and to make room for the reflecting prism. Inside the cell the light passes close to the edges of the single mirror, M1, to the first of the double mirrors, M2. The figure shows the simplest arrangement of the mirrors, in which the light is reflected from M2 to M1, then to M3 and finally out past the other edge of M1, giving four traversals of the space between the mirrors. By readjusting the double mirrors, the number of traversals may be increased to 24 without serious light losses.

The cell is mounted in the beam condenser on three adjustable screw feet. Figure 2 shows how it fits between the two right-hand lenses. The mounting screws are accessible through the three holes in the top. They extend through the cell housing to the base

INFRARED SPECTROPHOTOMETRY

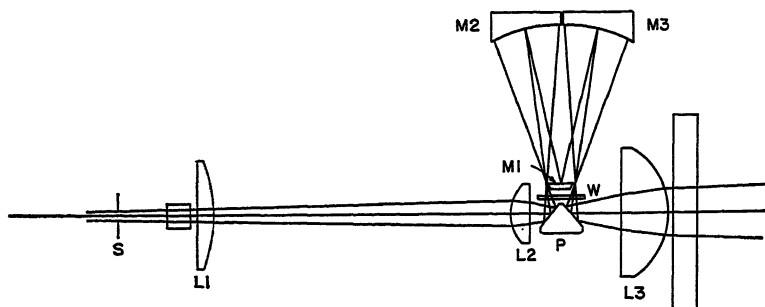


Fig. 1. Optical layout of microgas cell and beam condenser. S, slit image; L1, L2, L3, lenses of beam condenser; P, diverting prism; W, window of gas cell; M1, M2, M3, mirrors of gas cell.

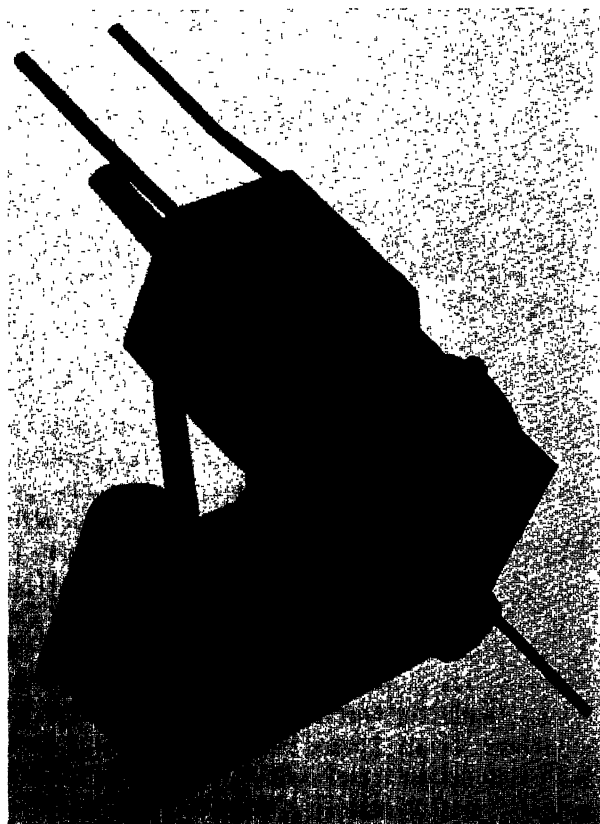


Fig. 2. Microgas cell in beam condenser.

of the beam condenser, where two of them rest in an aligning groove and the third in a slow motion worm operated by the knob in the bottom right corner. L1 is at the left, L2 in the knurled focusing mount in the

middle and L3 behind the cell. The sample inlet tube is the small one in the lower right, where it connects to the small end of the cell. The outlet is the large tube on the left. The other two tubes are the ends of a

cooling loop soldered to the outer jacket for circulating air or water. Inside the jacket a removable heater winding surrounds the main body of the cell containing the sample and the mirrors. The double mirrors are at the left, just ahead of the exhaust tube, adjustably mounted on six screws in a removable end plate. The single mirror and window are at the right near the middle lens. The cell and end plate are clamped together on "Teflon" gaskets by resiliently mounted screws.

The cell is built to be heated to 250°C, where it is limited by the "Teflon" gaskets. The body is "Monel," fastened with stainless steel screws. The glass mirrors should be satisfactory to 400°C if gold coated; the limit of the aluminized mirrors in different atmospheres has not yet been ascertained. Thirty watts input heats it to a steady temperature of about 145°C in an hour with 2.5 c.f.m. of air passing through the cooling tube. The temperature of the outer jacket is then around 45°C.

The performance of the cell and beam condenser has been tested in an IR-6 spectrometer.³ At 13.5 microns the beam condenser had a transmission of 60%. When the cell was put in, the six different path length settings from 16.7 to 100 cm were found to have the transmissions listed in Table 1. No extraneous transmission was observed between the different paths. The variation of transmission with wavelength is shown in the upper curves of Figure 3. The top curve is the I_0 of the spectrometer without the beam condenser, the middle one the transmission of the beam condenser alone, and the lower one the transmission of the beam condenser and gas cell set for 100-cm path length. In the lower two spectra the amplification of the spectrometer was increased by a factor of three to make up for the losses at the 1-meter path length. The middle spectrum is that of 0.16 ml of propane blown into the cell with air. The 3.4 micron C—H band is almost completely

TABLE 1. OPTICAL PERFORMANCE OF MICROGAS CELL AT 13.5 MICRONS

Traversals	Path Length, cm.	Transmission of Gas Cell, %	Transmission of Beam Condenser and Gas Cell, %
4	17	82	52
8	33	78	48
12	50	73	45
16	67	68	42
20	83	59	37
24	100	50	30

black, the 6.8, 7.25 and 13.34 bands are well defined and other weaker bands are detectable. Air was used for the I_0 curve. The lower spectrum is that of 0.16 ml of methane, where the bands around 3.3 and 7.7 microns are readily measurable. The comparison spectrum is the amount of gas remaining after the cell is purged with twice its own volume of air. The residual Q-branch of the band at 7.67 microns is still visible with a tenth of its former absorbance. The amount of methane present was then about 10 micrograms. From these and other measurements it is calculated that flushing the cell with its own volume of gas removes approximately 70% of the original contents.

The microgas cell and its beam condenser have been used in a Beckman IR-5 spectrophotometer² in conjunction with a Beckman model GC-2 gas chromatograph⁴ by flowing the effluent from the column directly through the cell following the thermal conductivity gauge. When the gauge indicated that an unknown peak had passed and should be in the cell, the flow to the column was stopped and the spectrum was measured. Figure 4 shows an application of this procedure to an unknown impurity that was detected in a previous chromatogram of absolute ethyl alcohol. The upper curve is the chromatogram of a 0.025 ml sample charged to the six-foot column packed with "Carbowax 1000" and operated at a temperature of 65°C. The flow to the column was stopped when the small peak before the main one

INFRARED SPECTROPHOTOMETRY

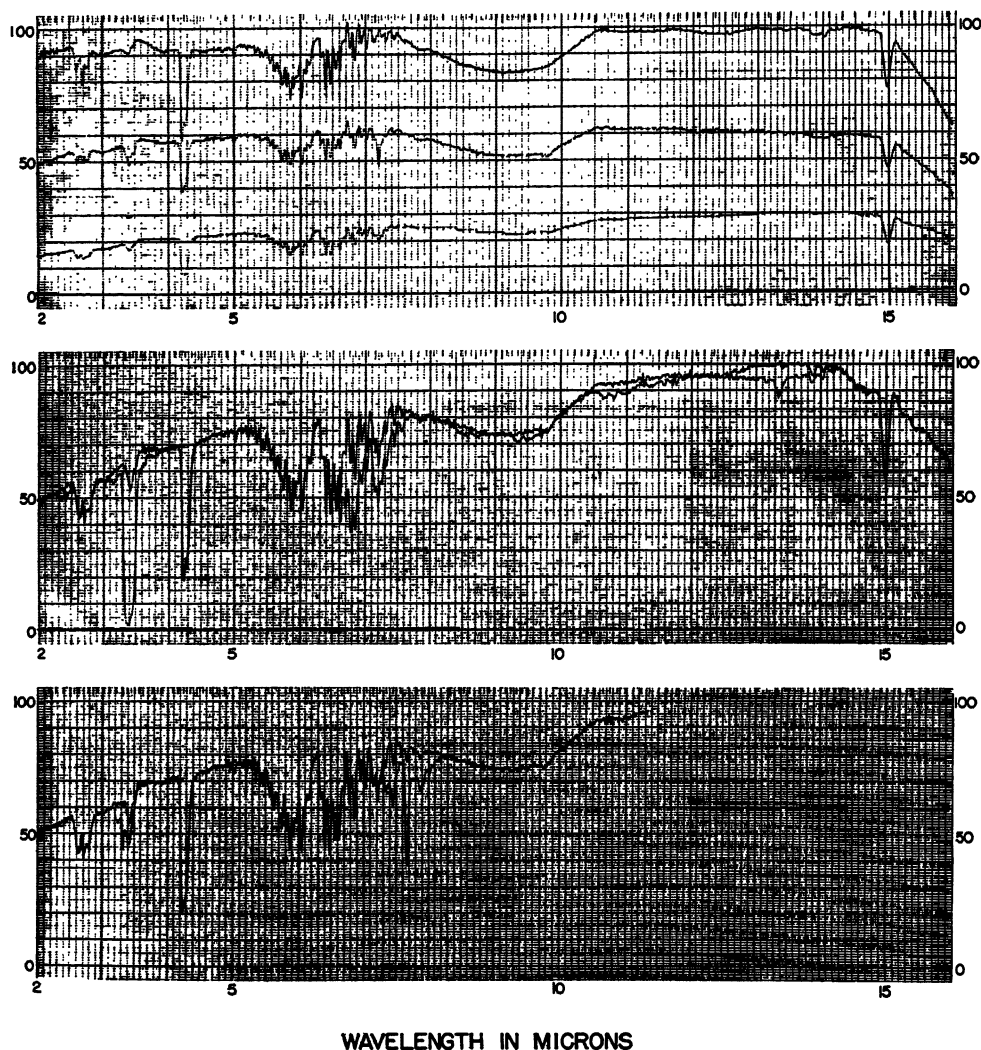


FIG. 3. Top spectra, in order I_0 of instrument alone, I_0 with beam condenser, and I_0 with beam condenser and one meter gas cell. Middle spectra, air and 0.16 ml of propane at one meter path. Bottom spectra, 0.16 ml methane at one meter path and same after flushing with two cell volumes of air.

was in the cell. The spectrometer was started and the spectrum shown in the bottom half of the figure was recorded. The strong P, Q and R branches of the 15-micron benzene band are readily recognized, as are the other strong bands at 3.3, 6.7, 8.2 and 9.6 microns. In addition to these there are extraneous bands at 5.7 and 8.4 microns. They have the wavelengths of strong bands in the spectrum of ethyl formate. As this should

come out of the column between benzene and alcohol where the chromatogram does not quite drop to zero, it is believed to be present. The amount of benzene is calculated to be 0.5%, that of ethyl formate 0.1%.

The microgas cell and chromatograph have also been used in an IR-4 spectrophotometer,⁵ where the higher performance of the larger instrument was used to com-

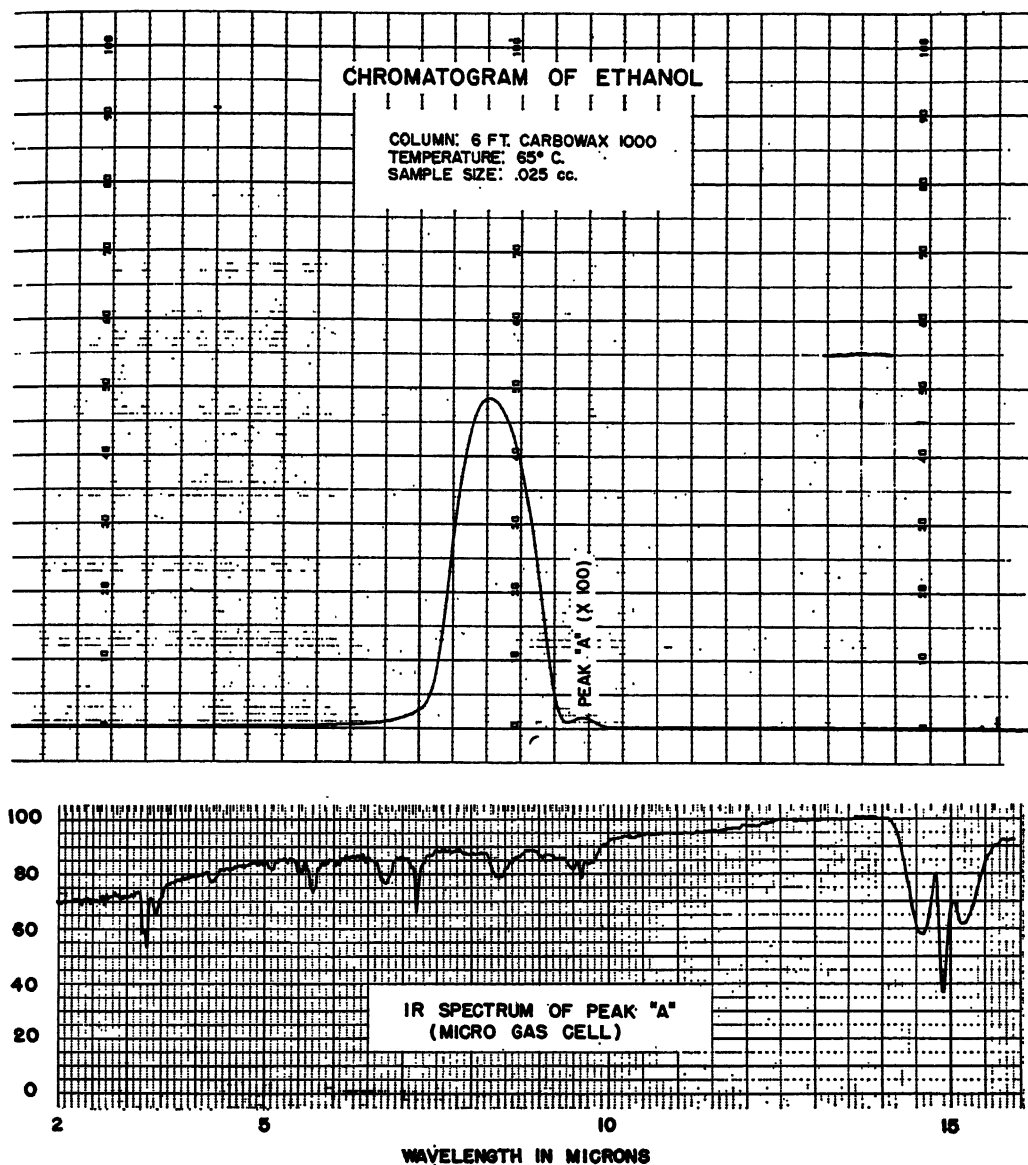


Fig. 4. Gas chromatogram of .025 ml absolute ethyl alcohol and infrared spectrum of Peak "A".

pensate for losses in the optical system. Figure 5 shows at the top the chromatogram of a 0.07-ml sample of impure toluene run on a 6-foot column packed with diethyl phthalate, operated with a flow rate of 50 ml per minute at a temperature of 125°C. In order below the chromatogram are the spectra of the first three peaks, A, B and C,

following the air peak. They have been identified as those of acetone, saturated hydrocarbon and benzene. Their concentrations were measured from the gas chromatogram as 0.04, 0.26 and 1.3%. The major peak, representing a toluene concentration of 97.8%, was recorded at 1/100 of the sensitivity used for the other peaks.

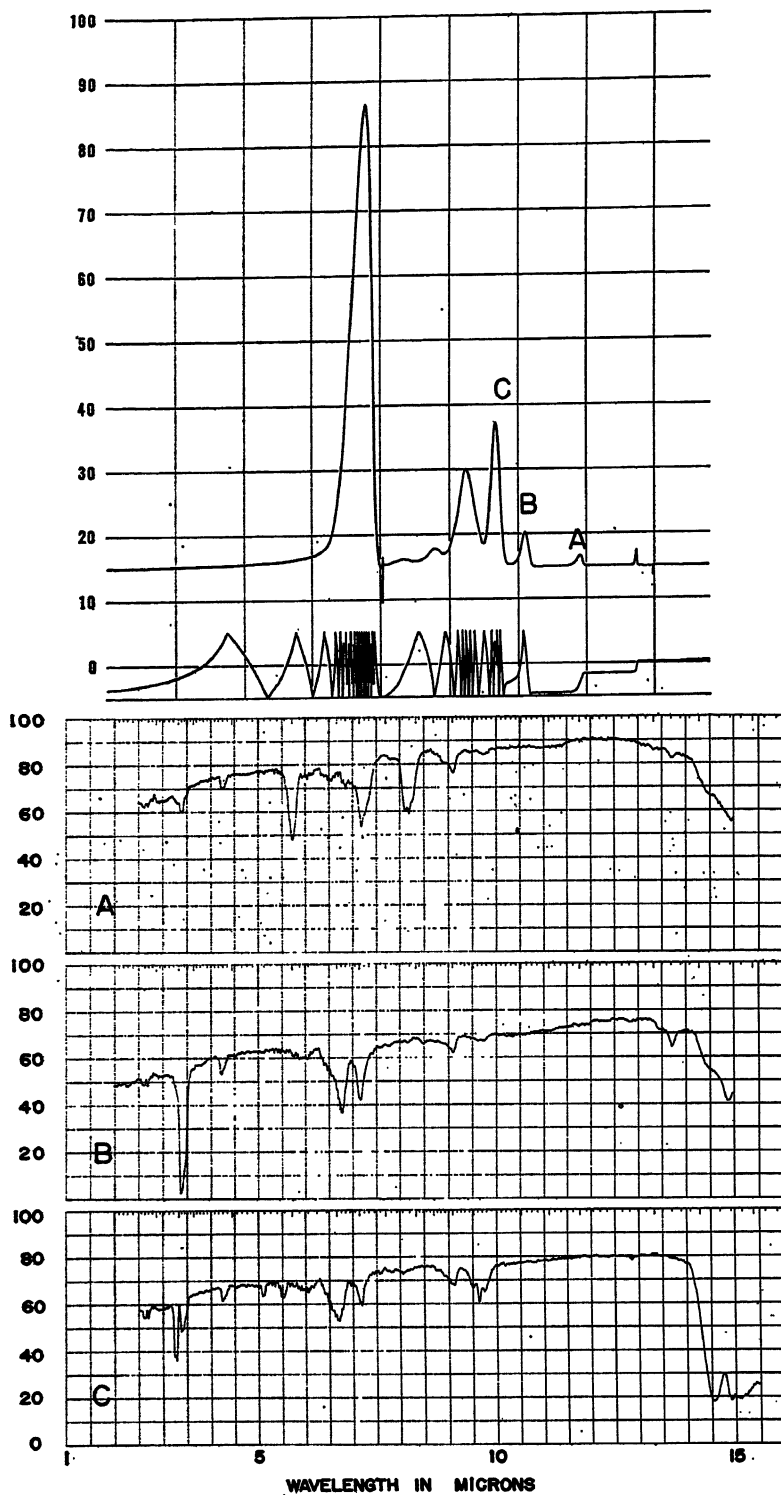


FIG. 5. Gas chromatogram of impure toluene with infrared spectra of first three peaks, A, acetone; B, saturated hydrocarbon; C, benzene.

To record the spectra of all the fractions continuously as they emerge from the column, the flow rate would have to be reduced to allow one scanning time per fraction. Then with a column that isolates a hundred fractions and with the 3-minute scan and 30-inch chart of the IR-4, five hours and 250 feet of chart would be required. More practical procedures are to slow down the column and record spectra only for the slowest fractions where identifications are more difficult or to record only when an unknown peak appears on the chromatogram. Further work is contemplated on this and on the use of delay lines to store the samples while the chromatograms are being examined.

The authors wish to thank Mr. James E. Stewart for making the measurements with the gas chromatograph.

REFERENCES

1. WHITE, J. U., *J. Opt. Soc. Am.*, **32**, 285 (1942).
2. WHITE, J. U., WEINER, S., ALPERT, N. L. AND WARD, W. M., *Anal. Chem.*, **30**, 1694 (1958).
3. WHITE, J. U., ALPERT, N. L. AND WEINER, S., *Rev. Sci. Inst.*, **29**, 511 (1958).
4. CARLE, D. AND DONNER, W., Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1957.
5. WARD, W. M., Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1956.

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MICROSAMPLING FOR SMALL INFRARED SPECTROPHOTOMETERS*

Numerous methods have recently been developed for measuring the infrared spectra of very small samples. Micro liquid cells¹¹ have been made to fit where the light beam is small, near the entrance slits of spectrometers. Silver chloride lens systems^{1, 2}

have been built to pass most of the light through a small sample at a reduced image of the slit. For further reduction of sample size, a number of reflecting microscopes and sampling systems^{3-10, 13-15, 23} have been devised. Special absorption cells in conjunction with a microscope^{5, 8} make it practical to measure the spectrum of approximately 1 γ of material in solution. Less than 1 μ l. of pure liquid may be measured without a microscope.¹² With the potassium bromide pellet technique and freeze drying of the samples,^{17, 19-21} the size of solid samples is reduced to 10 γ without the use of a microscope.¹⁸

All these methods have been used on commercial infrared spectrographs employing the standard 60 $\times$ 75 mm. prisms or larger, where there are instrumental adjustments that can easily be changed to correct energy losses or other difficulties resulting from the small sample size. Combining them with the recently announced²² small infrared spectrophotometers requires changes in the methods and equipment. They must be made compatible with the basic philosophy of the simple instruments that:

Accurate spectra be recorded as graphs of transmittance vs. wave length.

All spectra be made directly comparable by recording them on identical charts at the same speed, response time, and slit width.

Other types of measurements be possible by connecting additional equipment.

The operation be as simple and reliable as possible.

The cost be held to a minimum.

The basic unit on which most of the methods depend is a lens-type beam condenser. The device described here is such a unit that fits in the instrument's normal sample space. It uses three potassium bromide lenses to make an intermediate image of the entrance slit reduced five times and to reimage this again five times enlarged at the original focal point. All the light leaving the unit is

* Abridged version of paper in *Anal. Chem.*, **30**, 1694, (1958). By permission.

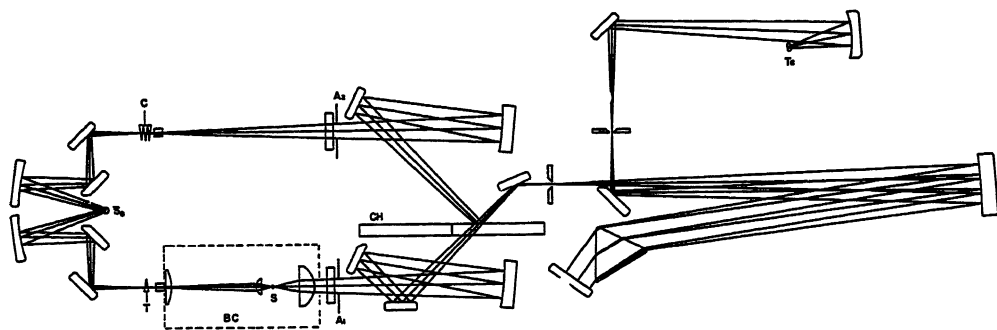


FIG. 1. Optical layout of beam condenser and spectrophotometer.
BC. Beam condenser *S₀.* Source *S.* Sample *Tc.* Thermocouple
T. Trimmer *C.* Comb *CH.* Chopper *A₁, A₂.* Apertures

then going along the same lines toward the same image points as it was when it entered. When the slits are widest, essentially all the rays pass through an opening 0.5×4 mm., giving over-all transmission of about 75 %, including reflection losses.

The optical arrangement of the spectrometer is shown in Figure 1. It is based on a Littrow monochromator with a 66° rock salt prism and a 40×50 mm. base. The collimator is a spherical mirror of 13.87-inch focal length used 8° off axis. The slits are 1 inch long, the exit slit being curved to compensate for the curvature of the image of the straight entrance slit due to the prism and the off-axis operation of the collimator. The whole monochromator is heated and thermostated to reduce the effects of temperature changes and to protect the rock salt windows. The wave length changes less than 0.02 micron for a 5°C temperature change.

The chopper, *CH*, and the other mirrors at the left of the monochromator form a symmetrical double beam system in which each beam has the same number of reflections from the same number of mirrors at the same angles. The source mirrors form images of the source close to the windows on the monochromator cover at the focal points of the double beam focusing mirrors. They in turn form virtual images of the source at infinity. The entrance slit is thus illuminated by a virtual source at infinity, and the ad-

vantages of coherent illumination are obtained. In addition, the whole area around the slit is illuminated, and there is no possibility of opening the slits so wide that they are not completely filled.

The source itself, *S₀*, is a "Nichrome" helix $\frac{3}{8}$ inch long and $\frac{7}{32}$ inch in diameter, electrically heated to a yellow color by a regulated power supply. A magnified real image of it appears in the prism, large enough to overfill the prism. To reduce scattered light in the monochromator, the overfilling is limited to the size that can just pass through the prism by a pair of apertures, *A₁* and *A₂*, in the two beams just inside the large cover and close to the two images of the prism.

The double beam focusing mirrors make real images of the entrance slit just inside the source cover at the position of the comb, *C*, in the reference beam and of the trimmer, *T*, in the sample beam. There is a reduction between the slit and its images that makes $\frac{7}{8}$ inch of comb height fill 1 inch of slit length. The arrangement of optics to put images of the slit near one end of the sample space and of the prism near the other limits the maximum size of the beams in the sample space to 0.16×0.86 inch on entering and 0.40×0.66 inch on leaving.

Following the monochromator, the light is focused on a thermocouple detector by a spherical mirror operated 14° off axis. This forms an image of the slit reduced five times,

which is reduced one half by a lens on the thermocouple, T_c , just in front of the 0.3×2 mm. target. Its resistance is about 2 ohms and its sensitivity 1 volt per watt.

The whole instrument operates on 250 watts of 115-volt, 60-cycle power. It automatically records a spectrum from 2 to 16 microns in approximately 16 minutes on a chart area 5×17.5 inches. The slits are cam driven. The actual resolution is about 85 % of that indicated by the spectral slit widths. For differential analysis, the slits may also be opened wider than the indicated values by means of an overriding manual control. The scanning rate is varied automatically in proportion to the spectral slit width to spend the same length of time on each resolvable interval.

Discussion

The performance of the instrument under the standard conditions is illustrated by the polystyrene film spectrum and the group of seven repeat spectra of iso-octane. The noise level is 1 %, the 100 % line is flat to ± 2 %, and the scattered light at 14.3 microns is 2 %.

The preferred place to put small samples is at the reduced image of the slit in the beam condenser. At this point the cross-section area of the beam is 2 sq. mm. or less, depending on the slit width. For a cell 0.1 mm. thick the volume of sample actually used is $0.2 \mu\text{l.}$; for a 0.025-mm. cell it is $0.05 \mu\text{l.}$ Samples of this size may be held and handled in liquid form in absorption cells like those of Davison¹² or Blout.⁸ Davison's cell, in which a groove has been cut in one window around the used area to hold the sample in the proper place by capillary action, has been used for minimum sample volume.

When a little more sample is available and some of it can be lost in dead space, Colthup's¹¹ self-filling capillary has proved convenient. With an area of 1×5 mm., its 0.025-mm. thickness gave it a used volume of $0.12 \mu\text{l.}$; its total volume, including filling tubes, was $10 \mu\text{l.}$ Its filling tubes had a vol-

ume much larger than the used part, but not too much more than that of thicker cells that were made for holding solutions.

These cells were used to measure the spectra of a number of essential oil samples, chosen to illustrate differences in the spectra of such materials and to show how they can be measured when only small quantities are available.

Phenyl ethyl alcohol sometimes occurs naturally as a minor constituent of rose oils, and in larger quantities it has also been used to adulterate them. Its monosubstituted phenol C—H out-of-plane vibrations at 13.4 and 14.3 microns and its primary alcohol vibration of 9.6 microns are characteristic.

The weakness of the aromatic bands in the rose oil spectrum indicates that the sample cannot contain more than a few per cent of the alcohol. Guaiac-wood oil, which is sometimes added to rose oils to mask the odor or other adulterants, has a spectrum with characteristic peaks at 8.8 and 11.1 microns. From the absence of sharp bands at these wave lengths, it is apparent that there is little if any of it present in the rose oil sample. Citronellol, on the other hand, has a spectrum so similar to that of the rose oil that it is likely to be one of the important constituents.

To measure the spectra of solid samples, a demountable die was built for pressing 1×5 mm. potassium bromide pellets. When the die is taken apart after pressing, the pellet can be deposited directly on the sample holder without intermediate handling. A sample size of 0.12 mg. seems to be approaching the limit for this method of mixing. The intensity of the spectrum is somewhat less than measurements on larger samples would predict, probably due to losses of sample on the walls of the plastic mixing container. For smaller samples the freeze drying technique described by Resnik¹⁸ and others is suitable. Samples as small as 10γ should be measurable by this technique.

A different kind of spectral measurement

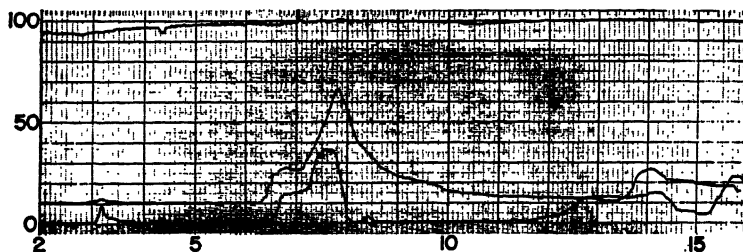


FIG. 2. Specular reflectance of boric oxide surface.

Top Aluminized mirror as reference.
 Center Freshly polished boric oxide surface with zero offset 10%.
 Bottom Fogged boric oxide surface.

is also possible, though at present without the use of the beam condenser. Infrared reflectance may be measured by inserting two small mirror surfaces into the sample space, arranged to reflect light to the polished surface of a sample and then back into its original path. The total path is lengthened $\frac{5}{8}$ inch, but this has not proved to be important when an aluminized mirror is used as a reflectance standard to determine the 100% line, as shown in Figure 2. This figure shows two spectra of a boric oxide surface measured at 30° angle of incidence. The upper curve is for the freshly polished surface, the lower one for the same surface lightly fogged by having been breathed on. The zero was offset 10% between the two spectra. The differences are due to hydration, indicated most clearly by the appearance of an OH reflection band at 3.2 microns.

REFERENCES

- ANDERSON, D. H., MILLER, O. E., *J. Opt. Soc. Am.* **43**, 777 (1953).
- ANDERSON, D. H., WOODALL, N. B., *Anal. Chem.*, **25**, 1906 (1953).
- BADGER, R. M., NEWMAN, R., *Rev. Sci. Instr.* **22**, 935 (1951).
- BARER, R., COLE, A. R. H., THOMPSON, H. W., *Nature*, **163**, 198 (1949).
- BLOUT, E. R., ABBATE, M. J., *J. Opt. Soc. Am.* **45**, 1028 (1955).
- BLOUT, E. R., BIRD, G. R., *Ibid.*, **41**, 547 (1951).
- BLOUT, E. R., BIRD, G. R., GREY, D. S., *Ibid.*, **40**, 304 (1950).
- BLOUT, E. R., PARRISH, M., JR., BIRD, G. R., ABBATE, M. J., *Ibid.*, **42**, 966 (1952).
- COATES, V. J., OFFNER, A., SIEGLER, E. H., JR., *Ibid.*, **43**, 984 (1953).
- COLE, A. R. H., JONES, R. N., *Ibid.*, **42**, 348 (1952).
- COLTHUP, N. B., WILLIAMS, V. Z., *Rev. Sci. Instr.*, **18**, 927 (1947).
- DAVISON, W. H. T., *J. Opt. Soc. Am.*, **45**, 227 (1955).
- ELLIOTT, A., AMBROSE, E. J., TEMPLE, R. B., *J. Sci. Instr.*, **27**, 21 (1950).
- FRASER, R. D. B., *Discussions Faraday Soc.*, No. 9, 378 (1950).
- GORE, R. C., *Science*, **110**, 710 (1949).
- MAKAS, A. S., SHURCLIFF, W. A., *J. Opt. Soc. Am.*, **45**, 998 (1955).
- NEUMANN, K., MATZ, G., *Chem. Ingr. Tech.*, **27**, 5 (1955).
- RESNIK, F. E., HARROW, L. S., HOLMES, J. C., BILL, M. E., GREENE, F. L., *Anal. Chem.*, **29**, 1874 (1957).
- SCHIEDT, U., REINWEIN, H., *Naturforsch.* **7b**, 270 (1952).
- SCHWARZ, H. P., CHILDS, R., DREISBACH, L., MASTRANGELO, S. V., KLESCHICK, A., Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., March 1956.
- STIMSON, M. M., O'DONNELL, M. J., *J. Am. Chem. Soc.*, **74**, 1805 (1952).
- WHITE, J. U., ALPERT, N. L., WEINER, S., Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., March 1957.
- WOOD, D. L., *Rev. Sci. Instr.*, **21**, 764 (1950).
- WRIGHT, N., HERSHEY, L. W., *J. Opt. Soc. Am.*, **37**, 211 (1947).

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MICROTECHNIQUES

With the development of present day chromatographic techniques for isolating microquantities of pure samples, the need for infrared microtechniques has become apparent. The use of these separation techniques is limited unless unequivocal identification of the constituents can be obtained. This is one area in which infrared microtechniques can play a large role.

Fortunately, recent advances in infrared equipment, such as beam condensing systems, microscope attachments, and scale expansion units, have enabled the identification of samples in the parts per million range. These accessories can be adapted to the microanalysis of gases, liquids, and solids by using specially designed infrared cells.

Critical analytical areas, such as air pollution studies, biological examinations, free radical investigations, surface chemistry problems, and chromatographic identifications of small quantities of materials, have benefited from the application of infrared spectroscopy to trace analysis. Infrared micro-sampling is a necessity in many biomedical investigations where only an extremely small sample is available for analysis. For example, the determination of the steroid hydrocortisone in human blood, which is present at a concentration of about 5 micrograms per 100 ml of blood, must necessarily require microanalysis. In this case infrared analysis provides positive identification.

Of the commercially available infrared spectrophotometers, none has any decided advantages in the analysis of microsamples. The microtechniques which have been reported in the literature can usually be adapted to any infrared spectrophotometer.

In this discussion the term micro will refer to quantities of materials less than 0.5 ml of gas (STP), 0.1 microliter of liquid, or 50 micrograms of solid.

Special Accessories and Equipment

Numerous accessories have been developed specifically for microinfrared analyses.

Devices such as beam condensing systems, microscope attachments, and scale expansion systems have become common infrared tools.

A beam-condensing system which optically reduced the size of the light beam from the source before it passed through the sample was reported by Anderson *et al.*¹ In this system a pair of silver chloride lenses, positioned to form the condensing arrangement, enabled the infrared analysis of samples in the 10 microgram range. White *et al.*²⁸ have designed an improved version of this beam condenser, using three KBr lenses which were capable of passing 75 % of the energy through a 0.5 to 4 mm sample area. Another beam condensing system,¹⁹ which uses an all-reflecting system of optics, provides a six-fold reduction in beam size. This system still maintains high energy levels when analyzing samples as small as 0.5 mm in diameter.

When extreme reduction in beam size is required to accommodate minute samples, the use of a reflecting microscope is necessary. A spectrophotometer with a microscope attachment is termed a microspectrometer. This microscope unit must be rigidly attached to the spectrophotometer and carefully aligned. It is usually mounted in the dispersed beam after the exit slit of the monochromator to minimize possible heating and photochemical effects in the sample. However, Blout *et al.*⁸ and Cole *et al.*¹¹ have described a reflecting microscope suitable for use in the sample beam of a double-beam spectrophotometer if some sample heating can be tolerated. Measurements have indicated that the sample temperature is raised to about 70°C. These microspectrometers are used for sample sizes in the fractional microgram range. An excellent discussion on the use of the combination of a microscope and a spectrophotometer is presented by Blout.⁷ Wood²⁷ also covers the theory and application of microspectrometers thoroughly.

Electronic ordinate scale expansion sys-

tems are recent modifications of infrared spectrophotometers. These scale expansion systems are versatile and convenient methods of increasing sensitivity based on the ultimate signal-to-noise capability of a double-beam spectrophotometer.

In a typical commercial instrument the optical wedge is used to null, or balance, any differences in the relative intensities of the sample and reference beams. Any change causes the wedge to move in a direction which increases or decreases the intensity of the reference beam the proper amount to restore balance. The wedge position is, therefore, proportional to the transmittance of the sample. A record of the wedge movement, hence sample transmittance, is obtained by coupling the recorder pen to the wedge, so that when the wedge moves the pen moves a proportional amount.

The ordinate scale expander changes the displacement of the pen relative to that of the wedge. At a setting of 1X on the expansion switch, the pen will travel the full length of the instrument transmittance scale for a full scale wedge displacement. At a setting of 5X, a full scale displacement of the wedge would produce a pen displacement equal to five times the length of the transmittance scale on the instrument, were this physically possible. Due to physical limitations of the instrument, the pen can travel only the length of the instrument transmittance scale which, at the 5X expansion now represents 20% transmittance. That is, the full transmittance scale covers from 100% to 80% transmittance. Thus absorption bands are increased five times in intensity at a setting of 5X.

The ordinate scale expander provides expansions of one, five, ten, and twenty times, corresponding to the ranges of transmittance units of 100%, 20%, 10%, and 5%, respectively.

Sample Types

Gases. The extensive use of gas chromatography and the high interest in odor

analysis have necessitated the development of methods for the analysis of small amounts of gases and liquids too volatile to be contained in infrared liquid cells.

In some instances the gases can be dissolved in a solvent (such as trapping the effluent gas from a gas chromatography column) and the infrared spectrum obtained by using a liquid cell. The microanalysis of liquids will be discussed in the next section.

In many cases it is more convenient to examine the material in the vapor state by using a gas cell. In microwork it is advantageous to have a cell with a minimum volume yet with most of the sample in the radiation beam. One method of obtaining this is to shape the gas cell so that it is the exact shape of the converging beam. This enables the entire sample to be in the beam, thus allowing maximum sensitivity.

The fabrication of folded-path cells permits the extension of the length of gas cells without proportional increases in volume. J. U. White *et al.*²⁵ have developed a miniature folded-path cell, to be used with a beam condenser, which provides an adjustable path length (17 to 100 cm) with a volume of only 22 ml. Its one meter path gives a length-to-volume ratio of 4.5 cm per ml, which is an increase of 50 to 100 times that of most standard 10 cm infrared absorption cells. Infrared spectra of samples as small as 0.01 ml (STP) can be obtained readily with this folded cell. Further, it can be used in conjunction with a gas chromatograph for identification of various fractions. Another desirable feature is that the temperature of the cell can be varied up to a maximum of 250°C.

A low-temperature microcell, developed by Stewart²⁶ for the analysis of small quantities of gases (0.03 to 0.3 ml STP) condensed at liquid nitrogen temperature, contains a silver chloride beam condensing lens. The sample is frozen in a thin film on a sodium chloride window maintained at about -182°C. The spectra of most frozen

gases closely resemble the spectra of the corresponding vapors; however, some exceptions have been noted.

An infrared cell was designed by Szymanski *et al.*²⁴ for collecting gas chromatographic fractions by condensing the effluent sample on a suitable absorbent. This cell can handle samples in the 0.02 ml range and no solvent or special handling techniques are required.

In the study of atmospheric contamination and trace quantities of gas in air, several long-path cells have been fabricated. A 40 meter path-length cell is now commercially available. Combined with the transmittance expansion effect of a scale expansion unit, an apparent path-length of 1600 meters—or one mile—is provided. The interior reflecting surfaces are gold-finished to minimize corrosive effects of samples. Stephens²¹ developed a cell with a path length of 216 meters for the measurement of gaseous contaminants in the atmosphere.

Liquids. The usual infrared cell for liquid samples has a 0.1 mm thickness and a volume of about 100 microliters. Using modified spacers, the volume can be reduced to 20 microliters; whereas a cell filled by means of a capillary tube, to keep dead space to a minimum, can contain as little as 2 microliters with a 0.1 mm path-length. Instrument modifications, such as masking the slits, will enable the analysis of 0.02 microliter of liquid. For example, Stewart²⁸ obtained the infrared absorption of the 13.7 micron band of toluene by using only 0.086 microliter of sample (5×10^{14} molecules).

Black *et al.*⁶ describe a relatively simple cell for handling liquids in the 0.08 microliter range. This cell consisted of a loop of thin platinum wire sandwiched between potassium bromide discs. A second sample cell was fabricated by drilling a small hole in a thin sheet of suitable material. This cell handled about 0.02 microliter of liquid analyzed as a thin film.

Another type of microcell, in which the sample fills an etched-out space between

polished-salt flats, was described by Davison¹⁸ and Friedel *et al.*¹⁸ This type of cell used a minimum sample volume ranging between 6 microliters for a cell of 0.1 mm thickness and about 0.2 microliter for a cell of 0.01 mm thickness.

The technique of microliquid analysis has gained prestige with the advent of gas chromatography. Molnar, *et al.*¹⁸ have used polyethylene micro-capillary tubes for trapping gas chromatography samples. These samples were analyzed directly with an infrared microspectrometer. The interfering bands from polyethylene were troublesome in the carbon-hydrogen regions; however, the polyethylene still allows enough windows for unequivocal identifications.

Microscope attachments are commonplace in microliquid analysis. Blout *et al.*⁹ described the apparatus and methods used for the infrared analysis of solutions containing about one microgram of solute. The absorption cell used was a piece of capillary tubing made of silver chloride with a bore diameter of about 0.075 mm. The cell was 1 to 1.5 mm long and was filled by means of a micro-pipette. A magnified image of the cell was projected on the entrance slit of the microspectrometer and the spectral data were recorded.

A similar capillary cell was fabricated by Black⁵ using the standard potassium bromide (KBr) pelleting technique. The cell is made by pressing a KBr pellet containing a piece of wire of a specified diameter. Removal of the wire gives a capillary cell of the desired diameter.

Of course, non-volatile liquid samples can be handled by using the potassium bromide technique, which is described in the following section on the analysis of solids.

Solids. Solids are most commonly analyzed as solutions, as suspensions in materials such as mineral oil (Nujol), or as potassium bromide pellets.

The analysis of a minute amount of a solid in solution requires a suitable solvent

(one in which the solute is soluble and which gives transmission windows) and the use of micro cells. If a satisfactory solvent cannot be found, the powdered sample may be suspended in Nujol or aluminum stearate and spread on a salt plate for analysis. Another possibility is to melt the sample and analyze it in the molten state. Low melting samples can be analyzed at room temperature, whereas high melting samples may be kept in the molten state by applying heat during the analysis.

Probably the most popular technique for analyzing solids is to press the sample into a KBr pellet. Such a method was described by Resnik, *et al.*²⁰ wherein the lyophilized sample was pressed into a pellet by means of a micro die. The advantage of this technique is that it requires no instrument modifications to analyze samples in the microgram range. By using an internal standard and the freeze drying technique, microgram samples can be analyzed quantitatively. The use of a special disc permits the sample to be analyzed directly in the die holder, thus eliminating transfer of the pellet. This technique is also applicable to the analysis of compounds eluted from paper chromatograms.

Kirkland¹⁸ described an evacuable, rectangular die for pressing KBr pellets to be used in the infrared analysis of microgram amounts of solids. No additional optical equipment, beam condensation, or special instrumental adjustment was required.

A KBr ultra-micro die described by Mason¹⁷ utilized vacuum alone to produce KBr pellets measuring either 0.5 or 1.5 mm in diameter. Pellets were precisely formed in the center of a 13 mm steel disc and remained in the disc during the infrared analysis. The 1.5 mm pellet was analyzed directly, while the 0.5 mm pellet was used in a beam condensing system to transmit enough energy.

Recently Bissett⁴ described a technique for fabricating a KBr pellet of any diameter

without using a special ultra-micro die. These pellets can be formed using most commercial or "homemade" dies.

Francis *et al.*¹⁴ described the modification of a double-beam infrared spectrophotometer which allowed the analysis of a film as thin as a monolayer in thickness on a metal mirror. The spectra obtained by this technique provided information about the orientation as well as the composition of sample films.

Surface coatings can be analyzed with any commercial spectrometer by employing a special reflectancy accessory. Dannerberg¹² describes this accessory in the infrared analysis of coatings which are 0.1 mil thick.

Applications

The field of infrared analysis has broadened considerably with the development of microsampling techniques for the study of small samples. The combined use of chromatography (paper, gas, and liquid) and infrared have far-reaching applications.

The analysis of small amounts of material is extremely useful in biological problems, such as the measurement of spectra of individual cells, of fibers, and of tissue sections. Such applications are presented by Barer *et al.*² and Coates *et al.*¹⁰ A conference, covering the biological applications of infrared spectroscopy was held by the New York Academy of Sciences. A detailed report of this meeting has been published.⁸

Air pollution studies, criminal investigations, biochemical research, odor analyses, and surface chemistry are but a few areas in which infrared microtechniques have direct applications.

Conclusions

Infrared microtechniques have not as yet reached their optimum usefulness in spectrophotometric analysis. The techniques have been developed for analyzing fractions of a microgram, but these techniques have not yet been applied routinely. The applica-

tion of these microtechniques will enhance infrared spectroscopy, particularly as it applies to the identification of trace constituents.

Accessories for infrared microtechniques, such as micro KBr dies, beam condensing systems, folded-path cells, microscope attachments, and ordinate scale expansion units, have been developed and are commercially available.

Micro gas samples can be analyzed by using special folded-path cells along with instrument modifications to enable infrared analyses of samples as small as 0.01 ml at STP.

Liquid samples as small as 0.0005 microliter can be studied with special cells in infrared spectrophotometers by using microscope and scale expansion accessories.

Solids in the fraction of a microgram range can be studied by using an ultra-micro die coupled with a beam condensing system.

In conclusion, infrared microtechniques are only now becoming available for routine analyses; they should make the infrared spectrophotometer the outstanding analytical tool of the future.

REFERENCES

1. ANDERSON, D. H., AND WOODALL, N. B., *Anal. Chem.*, **25**, 1906 (1953).
2. BARER, R., COLE, A. R. H., AND THOMPSON, H. W., *Nature*, **163**, 198 (1949).
3. BAUMAN, R. P., "Biological Applications of Infrared Spectroscopy," Vol. 69, Art. 1, p. 1-254, "Annals of the New York Academy of Sciences," ed. by Otto V. St. Whitelock, New York Academy of Sciences, New York, 1957.
4. BISSETT, F., BLUHM, A. L., AND LONG, L. L., JR., *Anal. Chem.*, **31**, 1927 (1959).
5. BLACK, E. D., *Anal. Chem.*, **32**, 735 (1960).
6. BLACK, E. D., MARGERUN, J. D., AND WYMAN, G. M., *Anal. Chem.*, **29**, 169 (1957).
7. BLOUT, E. R., "Microspectroscopy," Vol. I, part III, 2nd ed., p. 2179 "Technique of Organic Chemistry," ed. by A. Weissberger, Interscience, New York, 1954.
8. BLOUT, E. R., AND ABBATE, M. J., *J. Opt. Soc. Am.*, **45**, 1028 (1955).
9. BLOUT, E. R., PARRISH, M., JR., BIRD, G. R.,

- AND ABBATE, M. J., *J. Opt. Soc. Am.*, **42**, 966 (1952).
10. COATES, V. J., OFFNER, A., AND SIEGLER, E. H., JR., *J. Opt. Soc. Am.*, **43**, 984 (1953).
11. COLE, A. R. H. AND JONES, R. N., *J. Opt. Soc. Am.*, **42**, 348 (1952).
12. DANNENBERG, H., FORBES, J. W., AND JONES, A. C., *Anal. Chem.*, **32**, 365 (1960).
13. DAVIDSON, W. H. T., *J. Opt. Soc. Am.*, **45**, 227 (1955).
14. FRANCIS, S. A., AND ELLISON, A. H., *J. Opt. Soc. Am.*, **49**, 131 (1959).
15. FRIEDEL, R. A., PELIPETZ, M. G., *J. Opt. Soc. Am.*, **43**, 1051 (1953).
16. KIRKLAND, J. J. *Anal. Chem.*, **29**, 1127 (1957).
17. MASON, W. B., *Perkin-Elmer Instrument News*, **10**, No. 1, 1 (1958).
18. MOLNAR, W. S., AND YARBOROUGH, V. A., *Applied Spectroscopy*, **12**, No. 5, 143 (1958).
19. *Perkin-Elmer Instrument News*, **9**, No. 2, 4 (1958).
20. RESNIK, F. E., HARROW, L. S., HOLMES, J. C., BILL, M. E., AND GREENE, F. L., *Anal. Chem.*, **29**, 1874 (1957).
21. STEPHENS, E. R., *Applied Spectroscopy*, **12**, No. 3, 80 (1958).
22. STEWART, J. E., *Anal. Chem.*, **30**, 2073 (1958).
23. STEWART, J. E., "Beckman Application Data," Bulletin IR-88-MI, 1958, Beckman Instruments, Inc.
24. SZYMANSKI, H., POVINELLI, R., STAMIRE, D., AND LYNCH, G., *Anal. Chem.*, **31**, 2110 (1959).
25. WHITE, J. E., AND ALPERT, N. L., *Anal. Chem.*, **31**, 1267 (1959).
26. WHITE, J. U., WEINER, S., ALPERT, N. L., AND WARD, N. W., *Anal. Chem.*, **30**, 1694 (1958).
27. WOOD, D. L., "Infrared Microspectroscopy in Biological Research," Vol. 69, Art. 1, p. 194, "Annals of the New York Academy of Sciences," ed. by Otto V. St. Whitelock, New York Academy of Sciences, New York, 1957.

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MINERAL COMPOSITIONS AND STRUCTURES

While infrared analysis has been used extensively for the study of organic molecules, its application to the field of inorganic materials has been somewhat more limited, because the inorganic spectra have often proved less specific than the uniquely diversified organic spectra, and sampling difficulties with inorganic minerals have sometimes been

encountered. However, infrared analyses have been applied to the study of a variety of pure inorganic minerals and mixtures of minerals, and also to naturally occurring organic materials.

Because less work has been done in the inorganic field, the literature does not contain the extensive correlations of standard inorganic spectra that are available for organic materials. A prerequisite, therefore, to the application of infrared analysis to mineralogical problems involves collecting standard spectra of many different minerals, and making correlations of their absorption features.

Spectra have been obtained, between the wavelengths of 2 and 15 microns, for many of the common sulfate, carbonate, oxide, and phosphate minerals, among others. These spectra are characterized by fewer, and often broader, absorption peaks than are typical for the spectra of organic substances. In the spectra of some of the oxides and sulfides, no sharply defined peaks appear, but rather a generally diffuse level of absorption. For those minerals with complex anions, the anionic structure dominates the shape of the spectra, reflecting the covalent character of the anionic bonding. Thus, in the spectra of a series of carbonates with different cations, each has absorption at near 7, 11.5, and 14 microns, and in a series of sulfates, a strong absorption at near 9 microns and a secondary absorption near 15 microns. The different cations do not alter the over-all character of the spectra; however, minor wavelength shifts of the absorption peaks accompany different cations, and thus help to distinguish between the spectra of the series. Generally, the spectra of inorganic minerals are sufficiently distinctive so that the pure minerals may be identified, and because of the sharp, relatively few peaks, mixtures of 2 or more constituents may often be differentiated by the spectral features.

Standard spectra have also been obtained of silicate minerals of every structural class,

ranging from most tightly bonded silicates, the tectosilicates, in which the silicate tetrahedra are joined together to form 3-dimensional frameworks, to the least tightly bonded, like zircon, in which separate SiO_4 tetrahedral groups occur. Within the wavelength span 9 to 12 microns, most of the silicates show their major absorption band, which is due to the vibrations of the metal-oxygen bonds within the silicate tetrahedra. This is advantageous for characterizing the silicates as a group, as the absence of absorption within this wavelength span would indicate the absence of silicates. Conversely, it decreases the specificity of the spectra for analysis, because, although the major absorption peaks of many of the silicates are sufficiently distinctive for identifying the pure minerals, they would overlap in the spectra of a mixture of silicates, obscuring their individual features and increasing the difficulty of analysis.

For some silicates, the specificity of the spectra is increased by occurrence of secondary absorption peaks, outside the wavelength range of the main silicate absorption band, that are sufficiently sharp and distinctive for use in analysis. These occur mostly at wavelengths longer than 12 microns.

Also, the wavelength of the major absorption band may be correlated, in a general way, according to the type of tetrahedral bonding in the structure (the tectosilicates absorb at wavelengths between 9.2 and 10 microns, but less tightly bonded silicates absorb at progressively longer wavelengths until, for silicates such as zircon, in which the silica tetrahedra are isolated the absorption peak may occur at wavelengths as long as 12 microns), and also according to the amount of aluminum that has replaced silicon in the tetrahedra (thus, for the tectosilicates, the absorption peak wavelength undergoes a shift from near 9.2 microns for quartz and cristobalite, which contain no aluminum, to approximately 10 microns as the aluminum:silicon ratio in the tectosili-

icates increases to the maximum value of 1:1).

While the standard spectra usually cover the range from 2 to 15 microns, many of the inorganic minerals have sharp, intense absorption peaks at longer wavelengths, and the specificity of the spectra will no doubt be aided by extending their range. Much remains to be done in collecting and correlating the spectra of the inorganic minerals so that, similar to what has been done with organic compounds, these standard reference data will be available for analyses.

The infrared method can be usefully applied to a variety of specific mineralogical studies. In the identification of closely similar materials, such mineral pairs as the two crystal forms of KAlSi_3O_8 , orthoclase and microcline; two of the modifications of silica, quartz and cristobalite; the polymorphs of $\text{Mg}_2\text{Si}_2\text{O}_6$, enstatite and clinoenstatite; or the CaCO_3 polymorphs, calcite and aragonite, can be differentiated by their spectra. In the analysis of fine-grained rocks such as clays and shales, the small particle sizes of the minerals precludes the use of the polarizing microscope to identify the constituents; however, infrared spectra have been particularly useful in identifying the mineral constituents of such rocks. In connection with petroleum geology explorations, infrared spectra have been used to analyze the constituents of various surface samples, oil well cuttings, and cores; during drilling operations, penetration of drilling mud constituents into a formation has been conveniently followed by infrared analysis, since the comparison of the spectra of, for instance, a side-wall core of sandstone and of the drilling mud will indicate to what extent such constituents as calcite and kaolinite have been introduced into the sandstone in the course of drilling through higher formations. Infrared spectra are particularly useful to chart gradual changes in a series of materials by following the gradual changes in their absorption spectra. In one such study, spectra

were used to follow a series of channel samples of ores from along a contiguous mine wall; by correlating the successive changes in the spectra with the shift in the source of the sample, the effects of weathering and the oxidation states of the metallic constituents of the ores were charted.

In the study of solid-state syntheses of minerals, infrared spectroscopy is a particularly convenient method of diagnosing the progress of the reaction. The absorption spectra of the solid product, when compared with the spectra of the pure reactants, will indicate whether the product contains the synthesized mineral, or is merely a physical mixture of the reactants. By comparing the results of reactions under varying experimental conditions, the spectra will thus indicate the optimum conditions for synthesis of the mineral. Infrared analysis also provides a useful tool to study adsorption on the surface of a mineral, such as organic flocculants on clays, or hexanethiol on zincite—indicating, by interpretation of the spectra of the reaction product, the types of chemical bonding taking place on the mineral surface.

The major absorption bands of the inorganic minerals, while fewer in number, are generally more intense than those of most organic compounds. Accordingly, they have been found useful to determine very minor mineral constituents in mixtures. As little as one or two per cent of a carbonate in sedimentary rock, or of a polymorphic form in a mineral, may be determined. Less than one per cent of quartz has been detected in sedimentary rocks, (like numerous other minerals, the sensitivity of detection of quartz using infrared analysis is greater than with x-ray powder patterns—traces of quartz in clays were undetected from the x-ray pattern, but easily detected from the infrared spectra). Less than milligram amounts of most silicates can usually be detected from their spectra.

Quantitative analysis, in general, may be

made of a mixture of minerals, if each of the constituent minerals has a sharp, well-defined absorption band, in a region of the spectrum where there is a minimum of interference from the absorption bands of other constituents. For each of the minerals to be determined, a standard working curve is constructed, relating absorbance at the wavelength of the absorption peak with weight of pure mineral. The potassium bromide imbedding-window method of solid state sampling is most often used to make quantitative determinations of minerals.

Infrared analysis has also been of much value in the investigation of carbonaceous sediments. Spectra have been obtained of many different coals of differing rank and geographical location, of different constituents of coals such as anthraxylon, of various solvent extracts of coals, and of various asphaltenes, tars, and carbohydrate chars. These spectra have been studied to reveal information on the structural units in coal, and of the changes they undergo during the processes of coalification and carbonization. The highly complex spectra of these coal-type materials have thrown much useful light on their content, indicating coal structures to contain both single ring and condensed aromatic structures as well as aliphatic methyl and methylene groups, hydrogen-bonded hydroxyl (mainly phenolic), aldehyde or keto groups, and ether linkages. Many useful correlations have been made between the rank of the coal and the relative amounts of various unit structures present. Undoubtedly infrared methods will play an important part in future research into the nature of coals.

Other naturally occurring organic materials of geological interest, besides coals, that have been studied with infrared analysis include oils, petroliferous sandstones, carbonaceous solids impregnated in sandstones and shales, carbonaceous pellets, unknown organic coatings on rocks, asphaltic materials, and metalloorganic complexes con-

tained in petroleum. The spectra of all of these organic materials are usually too complex for complete analysis, since the various absorption peaks will often be superimposed and will obscure the true features of the absorption spectra. Analysis is facilitated, however, if further extractions are made of the constituents of the original material by such means of separation as the chromatographic column. The spectra are conveniently interpreted with the aid of the extensive correlations of absorption frequencies of organic groups, which appear in the literature, such as Colthup's correlation chart, and also the extensive catalog of hydrocarbon standard spectra compiled by such agencies as the American Petroleum Institute and the National Bureau of Standards-National Research Council. The spectra reveal possible information on the origins and structures of these naturally occurring organic materials, and of their various relationships when enclosed within a stratigraphic unit.

Infrared analyses, in conjunction with x-ray and chemical analyses, have contributed to the study of the crystal structures of inorganic minerals. The method has been particularly useful when applied to the study of hydroxyl and molecular water groups in crystals. Unlike x-ray analysis, which is complicated by substances that readily gain or lose water of hydration, the intensity of the separate absorption peaks of hydroxyl and molecular water groups, and the shape and vibrational frequency of the hydroxyl absorption peak, give direct indication of the relative amounts of OH and H₂O present, and of the extent of hydrogen bonding in the crystal. One such application involved study of a new silicate mineral, coffinite, in which the very small size of the coffinite crystallites and their association with other fine-grained minerals and with organic matter precluded separation of the pure mineral; adequate chemical characterization could not be made, and attempts to synthesize the pure mineral failed. From the infra-

red spectra, however, it was possible to establish the substitution of hydroxyl groups for oxygen in the silicate tetraheda, and infer the chemical formula as $U(SiO_4)_{1-x}(OH)_x$. In another structure study, concerned with the nature of the water contained in volcanic glasses, infrared spectra that were obtained of samples of perlite indicated that perlite contains dominant hydrogen-bonded OH and H_2O , with some monomeric OH, and little mechanically-trapped water, and this information was used further to infer the architecture of the perlite structure. Similarly, in a study of montmorillonites and other clays of lesser base-exchange capacity, the variation in the shape and intensity of the OH and H_2O absorption bands with variation in hydration were interpreted to show the degree of hydrogen bonding in the clays, and also to rank the water-uptake according to the cation in the clay.

With the use of polarized radiation, further structure studies may be made. If a single crystal of the mineral is oriented with respect to the incident light, then it is possible, by comparing the relative intensities of absorption of the bands with the radiation plane-polarized in two perpendicular directions, to determine the spatial direction of atomic groups within the crystal. For layer structures, such as clays, polarized radiation is particularly useful for determining the crystallographic anisotropy character of the mineral. In mica, the absorption spectra obtained with polarized light were used to determine the spatial orientation of the OH oscillator; in a study of brucite, the polarized spectra indicated that the size of the unit cell of brucite, and the position of the hydrogen atoms had been incorrectly assigned from x-ray data (thus demonstrating the much greater sensitivity of the infrared method, compared to that of the x-ray method, in ascertaining the positions of hydrogen atoms in crystals).

REFERENCES

1. DUVAL, CLEMENT AND LECOMTE, JEAN, *Compt. Rend.*, **234**, 2445 (1952).
2. HUNT, J. M., WISHERD, M. P., AND BONHAM, L. C., *Anal. Chem.*, **22**, 1478 (1950).
3. HUNT, J. M. AND TURNER, DANIEL S., *Anal. Chem.*, **25**, 1169 (1953).
4. KELLER, W. D. AND PICKETT, E. E., *Am. J. Sci.*, **252**, 87 (1954).
5. KELLER, W. D., SPOTTS, JOHN H., AND BIGGS, DONALD R., *Am. J. Sci.*, **250**, 453 (1952).
6. KENDALL, D. N., *Anal. Chem.*, **25**, 382 (1953).
7. LECOMTE, JEAN, *J. Chem. Phys.*, **50**, C53 (1953).
8. LIPPINCOTT, E. R., VAN VALKENBURG, A., WEIR, C. E., AND BUNTING, E. N., *J. Research, N. B. S.*, **61**, 61 (1958).
9. SIMON, EVAN, *J. Am. Ceram. Soc.*, **40**, 150 (1957).
10. SIMON, IVAN AND McMAHON, H. O., *J. Chem. Phys.*, **21**, 23 (1953).
11. STIEFF, L. R., STERN, T. W., AND SHEERWOOD, A. M., *Am. Mineralog.*, **41**, 675, (1956).
12. VERGNOUX, A. M., *J. Chim. Phys.*, **50**, C75 (1953).

ROBERT G. MILKEY

MINERALS AND ROCKS

The use of the infrared absorption spectrophotometer for structural studies and analysis in organic chemistry has been well known for a long time. Its use in the inorganic and mineralogical field is of more recent origin and has not as yet been fully exploited. Absorption curves can be obtained with samples representing rocks, or mixed or individual minerals. The spectra obtained can be used for identification, quantification or structural studies.

Sample Preparation

Hunt (1950) described the use of deposited films of finely divided minerals on rock salt windows for infrared studies. Miller and Wilkins (1952) compiled an excellent catalog of inorganic spectra obtained using mineral oil mull techniques. The value of the infrared spectra of minerals has been further demonstrated by a number of other workers in the

field who used one or the other of these techniques or modifications of them.

The deposited film technique yielded excellent spectra beyond about 4 microns, but was relatively tedious and time consuming. There was a further possibility of modification of the composition of a mixture because of techniques of gravity separation of the components. The mineral oil mull technique suffered from the presence of interfering absorption bands and lack of the desired degree of control for quantitative purposes.

In recent times the KBr-pellet technique described independently by Stimson and Schiedt (1952) has become widely used for preparing samples for the infrared study of materials for which no suitable solvent can be found. Minerals, of course, fit into this category. The KBr-pellet technique has been shown to be a most satisfactory method for handling rock and mineral samples for infrared analyses.

Excellent infrared absorption spectra of minerals can be obtained with KBr discs containing about $\frac{1}{4}$ per cent of the sample in question. A well tested method of preparation involves hand grinding 10 mg of the sample with 10 drops of absolute alcohol in a 60 mm mullite mortar, until the alcohol evaporates. This reduces the grain size to below 5 microns (about 50 % minus 2 microns) and minimizes effects due to grain size. Two and one-half milligrams of this preground sample are added to 1.00 gm of infrared quality KBr and blended in a dentist's amalgamator. Enough of the blend is weighed out to form a disc of the desired thickness (1 to 1.5 mm) and pressed in a vacuum die. About 65 tons pressure per square inch is adequate to obtain permanently clear discs. It has been found necessary to grind the samples under alcohol because the structure of many minerals, particularly those containing OH groups in the lattice, can be altered in a few minutes by vigorous dry grinding. If careful, consistent preparatory grinding, coupled with adequate

blending, is followed, linear calibration curves for quantitative analysis can be obtained using standard mineral specimens.

Analysis of Rocks

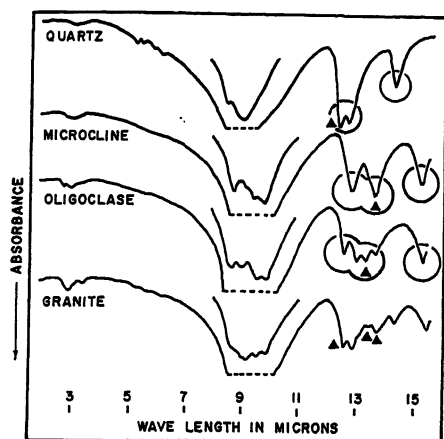
The infrared method has several distinct advantages in determining rock composition. The sample can be taken directly in powdered form from an assay pulp (at minus 200 mesh) as submitted for wet chemical analysis; thus, the petrographic data deduced from the infrared analyses are obtained from the same sample undergoing chemical analysis. The same care which goes into all stages of collection and preparation of assay samples, therefore, is available for the preparation of the sample for infrared analysis. The method is admirably suited to the petrography of fine grained or even cryptocrystalline rocks; in fact, excellent spectra can be obtained with samples that would be judged amorphous by x-ray diffraction. The petrography of a sample can be determined even if that sample is a small grain, a rock chip or the bulk integration of many hundreds of feet of drill core.

When samples are properly prepared, the infrared technique is unaffected by the grain size of the particular minerals, and can greatly assist in rapid quantitative determinations of minerals. Coupled with thin- and polished-section study of the rocks, and other instrumental methods, this approach greatly improves the over-all analysis. The contents and types of many clays, hydrated minerals, carbonates, and silicates in rocks can be easily determined by infrared analysis.

In Figure 1 the spectra of the three primary minerals found in a typical granite are shown. Absorptions that are most useful for identification of these constituents are circled. By measuring the absorption given by the rock at the points marked by triangles and applying simultaneous equations, the percentages of those constituents present in a granite sample can be determined. With these fundamental determinations, almost all

acid igneous rocks may be correctly categorized since, in general, the quantitative determination of the black ferromagnesian and other accessory minerals is not essential to the classification of these rocks.

For some types of minerals such as carbonates the infrared method is extremely sensitive and can be used for the detection and measurement of quantities down to 0.5 per cent. For others such as montmorillonite and biotite, its value is restricted to work in

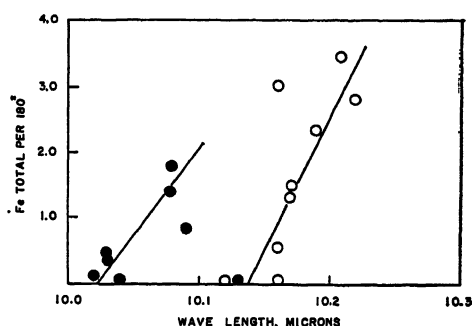


(*Economic Geology*, 1959)

FIG. 1. Absorption curves of major constituent minerals of standard granite sample. Bands marked ▲ were used for quantitative analyses.

TABLE 1. ESTIMATED INFRARED LIMITS OF DETECTION OF MINERALS IN TYPICAL ROCK ENVIRONMENTS

Mineral	Sample Type	Lower Limit of Detection
Carbonates	Any rock	0.5%
Quartz	Any rock	1
Plagioclase (An ₅ to An ₂₅)	Any rock	5
Orthoclase	Granite	5
Sericite	Alteration	15
Biotite	Shist	50
Augite	Diorite	10
Kaolinite	Alteration	3
Montmorillonite	Alteration	25
Alunite	Alteration	3
Jarosite	Alteration	3
Chlorite	Alteration	15



(*Analytical Chemistry*, 1959)

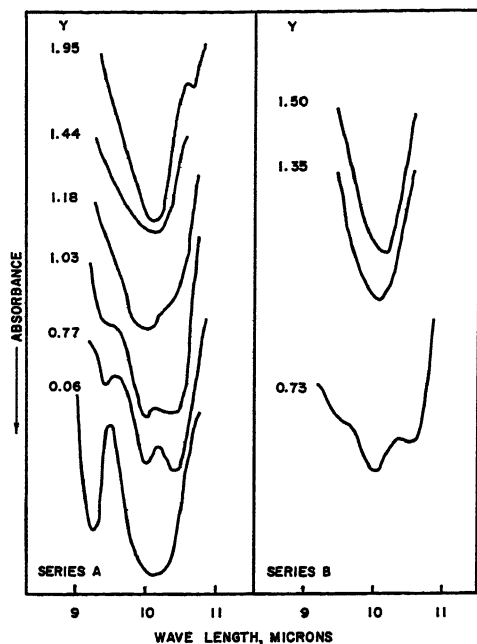
FIG. 2. Variation in the position of 10-micron absorption band with increasing substitution of iron for magnesium in the octohedral position in a series of chlorite minerals. Open circles, high aluminum series; filled circles, low aluminum series.

higher concentration ranges of the order of 25 per cent and above. A few minerals, such as pyrite, give no absorption in the rock salt region (2–15 microns) and such broad shallow absorptions at longer wavelengths that they could only be identified at near 100 per cent concentration. Estimated limits of detection for a number of minerals in typical rock environments are listed in Table 1. These estimates are based on the use of ordinary instrumentation and preparation methods. It may be possible to exceed them by using special techniques.

Structural and Compositional Studies of Minerals

A feature of the infrared spectra of minerals of great potential value is that small structural or compositional changes cause distinct spectral changes either as wavelength shifts or curve shape modifications or both. These types of phenomena are illustrated in Figures 2 and 3 for a series of chlorite minerals. Not only is the degree of iron substitution shown by the infrared spectra of these minerals but there is indication of a possible structural change as the aluminum to silicon ratio changes.

It is often possible to fit a sample into a



(*Analytical Chemistry*, 1969)

Fig. 3. Infrared absorption curves in the 9-11 micron region showing the effect of decreasing ratio (Y) of substitution of Al for Si in the tetrahedral positions in the crystal lattice of the magnesium chlorite series.

Series A. Low Fe substitution.

Series B. High Fe substitution.

general classification on the basis of the overall curve shape and then to further refine the identification on the basis of the specific positions at which absorption bands occur. Carbonates and sulfates, for instance, have very characteristic spectra. The carbonates invariably give a major absorption band in the vicinity of 7 microns and the sulfates give a major band at about 9 microns. Other absorption bands are present at longer wavelengths which are more specifically related to the particular cation in question for both carbonates and sulfates. Where solid solutions exist, the positions of these absorption bands generally lie between those of the extreme members of the series. This has been reported by Thompson and Wadsworth (1957) for plagioclase feldspars, and has

been observed for carbonates, olivines and garnets as well.

Infrared analysis as applied to minerals is a new but powerful analytical tool; however, there is much yet to be learned. Several successful applications have been made to problems in bulk mineralogy of rocks and metallurgical products, but the most favorable area lies in its ability to detect slight chemical changes in minerals. Solid solution phenomena are widespread in mineralogy. When coupled with x-ray diffraction for crystal structural analysis, the infrared method provides a sensitive measure of the chemistry involved.

W. M. TUDDENHAM
R. J. P. LYON

NEAR INFRARED SPECTROSCOPY (with complete bibliography)

This article is divided into two parts: a brief survey of the current status of near infrared spectroscopy and a more detailed study of those weak molecular interactions responsible for the "polarity" of solvents.

If we may agree for the moment that the near infrared region extends from the visible to about 3.5μ , the only distinction for this region is in the instrumentation used. There are four aspects of this instrumentation that deserve mention. (1) An ordinary incandescent source radiates a maximum amount of energy in this region so that most instruments are not "energy limited." Also stray light can be kept very low. (2) The lead sulfide detector useful throughout the near infrared region is very sensitive and rapid responding, and yields a large output signal. (3) Quartz prisms and gratings of high dispersion permit high resolution. Commercial instruments are now available with a resolving power of 5000 or more and custom built instruments have achieved values as high as 150,000. (4) Long, accurately measured, and permanently sealed cells can be

used, eliminating one of the troublesome variables in quantitative analysis.

There is little that can be considered distinctive about the absorption processes that occur in the near infrared region. The absorption bands are very numerous and narrow but arise largely from the vibrations and rotations of molecules. A few electronic transitions occur. The prime distinction is that most of the vibrations responsible for near infrared absorption arise from motion of a hydrogen atom in the absorbing molecule. Below 2.7μ all the absorption bands are due to overtones of hydrogenic stretching vibrations or combination bands involving a hydrogenic stretching motion with other modes of vibration in the molecule. These vibration bands are interpreted in the same way as other bands in the conventional rock salt region.

One of the best ways of summarizing a field is to catalog its literature. A relatively large number of papers are currently appearing in the scientific journals. Table 1A attempts to classify these papers. Only those papers primarily concerned with the near infrared portion of the spectrum are considered here. The papers fall into three general types (1) analytical, (2) instrumental and (3) spectral interpretation of some molecular property.

The analytical papers may be further categorized as shown in Table 2B. In almost all cases the analyte (components being analyzed) is characterized by an OH, NH or CH group. Water has been analyzed in glycerol, hydrazine, freon, organic films, acetone and fuming nitric acid. Absorption bands at 2.76, 1.90 and 1.40 microns are used depending on the concentration of the analyte. Where interferences from other absorption bands are severe or where very low concentrations of water are being studied some investigators have extracted the water with glycerol or ethylene glycol. Often the contaminating material has very low solubility in these polyhydroxy compounds while water

TABLE 1A

Analytical.....	30
Instrumental.....	17
Band Assignment.....	20
Hydrogen Bonding.....	38
Physical Chemistry.....	49
	—
	154

TABLE 1B

Water.....	10
Phenols, Alcohols.....	5
Amines and NH.....	4
CH.....	4
Emission.....	4
Other.....	3
	—
	30

is extracted quantitatively. In fact anhydrous glycerol is an excellent drying agent for many organic compounds. Several papers cover the analysis of deuterated and tritiated water.

Phenols, alcohols and carboxylic acids have also been analyzed utilizing these characterizing OH absorption bands.

The strong NH absorption bands of amines are located in a portion of the spectrum where few other groups absorb intensely, and are susceptible to good quantitative and qualitative analysis.

While most of the near infrared absorption bands of organic compounds arise from CH groups, relatively few analyses utilize this fact, probably because they are often insufficiently characteristic. However, papers determining unsaturation, terminal epoxides and aldehydes may be found.

Near infrared absorption spectroscopy has also been used for the determination of oxygen and carbon dioxide in the atmosphere.

A few papers on emission spectroscopy in the near infrared have appeared. A number of metallic oxides in flames emit sharp bands.

Table 1C gives a breakdown of papers on physical chemistry. The Physical chemists

INFRARED SPECTROPHOTOMETRY

TABLE 1C

Solvent Shifts.....	18
Structure.....	10
Coordination.....	6
Adsorption.....	4
Refractive Index.....	3
Other (Dichroism, Reactivity etc.)...	8
	49

TABLE 1D

J. Chem. Phys.....	38
J. Opt. Soc. Amer.....	18
Anal. Chem.....	17
Spectrochim Acta.....	15
J. Amer. Chem. Soc.....	12
J. Phys. Chem.....	11
Other (24 Journals).....	43
	154

have made widespread use of the near infrared region for studying hydrogen bonding, coordination and dipolar interactions. In addition, studies of absorption behavior on silica gel have been made. Also measurements of refractive index, dichroism and rotatory dispersion have been made. A few very interesting correlations between spectral band position and chemical reactivity have been reported.

Table 1D lists the journals in which most of the papers on near infrared spectroscopy appear (1955-58). While the lion's share have appeared in the *Journal of Chemical Physics*, the number in 1958 seems to have definitely decreased. The new Russian *Optika i Spektrosk* has a number of good papers in it.

The literature survey has revealed that the greatest interest in near infrared spectroscopy has been evidenced by those investigating hydrogen bonding and solvent shifts. Indeed few papers on near infrared spectroscopy can be found that do not mention the hydrogen bond. In my own opinion, the term has been used too loosely and should be reserved for quantum interactions wherein the hydrogen atom is discretely, if

momentarily, bonded to two other atoms. The four major types of molecular interactions are: Dipolar, Hydrogen Bridge, Coordinate Bond, Covalent Bond. Only the weakest of these, the dipolar interaction will be mentioned here.

When high resolution is available one may easily observe that the exact position and shape of a solute absorption band is dependent on the solvent used. Few solvents behave exactly the same way in this regard. Fig. 1 shows the type of spectra obtained with a Beckman IR-7 Spectrophotometer. The upper spectrum is of acetylene in the vapor state. While one would expect only one vibration-rotation band, the C—H stretching mode ν_3 , an analysis of the rotational components reveals that a second band, $\nu_2 + \nu_4 + \nu_5$, is present. The high intensity of this second band can only be explained by Fermi resonance. When dissolved in organic (and inorganic) liquids the bands change considerably, losing all their rotational fine structure. In the very non-polar fluorinated solvents the bands are shifted very little from the vapor state. With increasing solvent polarity the bands move to lower frequencies. In carbon tetrachloride, which generally produces the sharpest solute bands, there is evidence for the two bands ν_3 and $\nu_2 + \nu_4 + \nu_5$. The greater perturbation produced by the more polar substituted benzene solvents

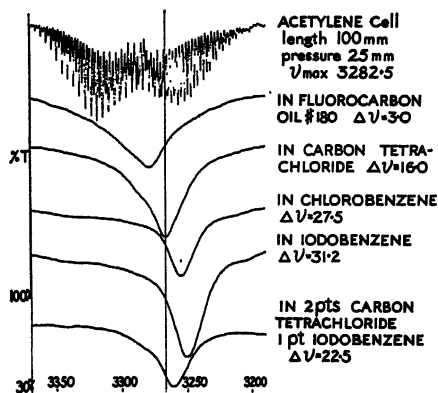


FIG. 1. Acetylene in various solvents, fundamental.

evidently affects these two bands differently, reducing Fermi resonance and thus greatly suppressing the intensity of the combination band.

Fortunately many near infrared solute bands arise from one vibrational motion and are simpler to interpret. The first overtone of the acetylene CH stretching band is an example. Fig. 2 reflects these simpler bands. The solution bands are reasonably symmetrical and the frequency of the maximum as well as the breadth at half maximum absorbance can be measured with precision. Table 2 gives these values for a number of solvents. Of particular interest is the very small perturbation of the perfluorokerosene and the large magnitude of the shift in methylene iodide. Carbon tetrachloride generally produces the narrowest bands. This is attributed to the more homogeneous dielectric field of this symmetrical molecule. The 1-chlorodecane solvent produces an unsymmetrical solute band attributed to the presence of the two perturbing influences of the C-Cl and C-H solvent dipoles. The large breadth of the solute band in *n*-hexane is unusual and merits further study.

Solvent shifts of the above type have been interpreted as due either to hydrogen bonding or the dielectric field of the solvent. The equation (in a simplified version) relating the solvent dielectric continuum to the perturbation is called the Kirkwood-Bauer-Magat equation:

$$\frac{\Delta\nu}{\nu} = C \left(\frac{\epsilon - 1}{2\epsilon + 1} \right) \text{ or } \\ = C \left(\frac{n^2 - 1}{2n^2 + 1} \right)$$

Values of C in this equation for hydrogenic stretching vibrations have been reported to be between 0.02 and 0.111, depending on the "acidity" of the hydrogen. These C values have been determined assuming that such solvents as cyclohexane and carbon tetrachloride are ideal non-polar solvents which can be considered as homogeneous

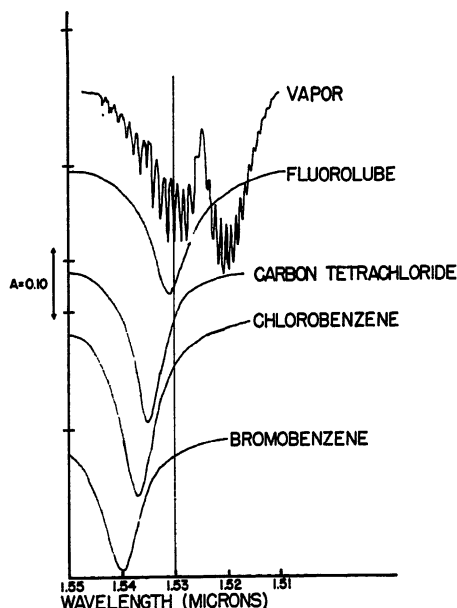


FIG. 2. Acetylene in various solvents, first overtone.

TABLE 2. 6500cm⁻¹ ACETYLENE BAND IN VARIOUS SOLVENTS

Solvent	Shift	Breadth
Vapor	$\nu = 6557 \text{ cm}^{-1}$	
Perfluorokerosene.....	12	41
Fluorolube	25	40
η -Hexane	30	54
Carbon Tetrachloride...	42	30
1-Chlorodecane	48	47
Chlorobenzene.....	61	36
Bromobenzene.....	64	39
Methylene Iodide.....	82	40
35% Bromobenzene.....	37	51
In Fluorolube		

dielectrics. This appears now to be a faulty assumption.

To test the Kirkwood-Bauer-Magat equation the OH band of phenol was studied in several solvents. The C value reported in the literature for phenol is 0.050. The frequency and band width of the OH band in solution are given in Table 3. The fluorocarbon solvent perturbs the band very little and the K-B-M-C value using a refractive index value of

INFRARED SPECTROPHOTOMETRY

TABLE 3. BAND POSITION-PHENOL SOLUTIONS

	ν_m	ν_d	$\Delta\nu$
Vapor.....	3655.8		
Fluorocarbon 180.....	3644	15	12
CCl_4	3613	17	43
Chlorobenzene.....	3577	44.6	79
Iodobenzene.....	3567	45.0	89
Methylene Iodide.....	3550	63	106
Benzene.....	3558	36	98

1.301 is only 0.021—considerably less than the accepted value. The C value for the other solvents except carbon tetrachloride is greater than 0.050 and the conventional interpretation would classify these as hydrogen bonded systems.

If the C value of phenol is actually 0.021 or less (i.e. the contribution to the perturbation attributable to a dielectric continuum) then carbon tetrachloride cannot be considered non-polar. A degree of specific interaction between the C-Cl moments of the carbon tetrachloride and the OH group of phenol exists. Fig. 3 confirms this. This spectrum is of a solution of phenol (0.004*M*) in a mixture of 6% by volume carbon tetrachloride and 94% Fluorocarbon 180. The Fluorocarbon 180 is a very poor solvent and saturates with this much carbon tetrachloride at room temperature. In order to assure one phase, the temperature of the solution was raised to about 35°C. Analysis of this spectrum reveals two bands at 3644 and 3626 cm^{-1} . The lower frequency band may arise from phenol molecules the OH groups of which are adjacent to carbon tetrachloride molecules. If so, the band is more intense than one would expect on the basis of the concentration of carbon tetrachloride. A preferential interaction between phenol and carbon tetrachloride is indicated.

Phenol in a mixture of cyclohexane and Fluorocarbon oil 180 produced a very similar appearing spectrum except that the lower frequency component had a greater half width.

Assuming that some interaction occurs

between phenol and carbon tetrachloride, one may ask if this is an example of a weak hydrogen bond. If the hydrogen bond is a quantum interaction wherein an electron donor contributes electrons to an acidic hydrogen it seems unlikely that highly electronegative halogens could form a hydrogen bond. Further quantitative measurements are needed to decide this point. Unfortunately, the poor solubility of most compounds in perfluoro solvents makes their quantitative study difficult. Consequently carbon tetrachloride was chosen as a solvent.

Fig. 4 shows the spectrum of phenol in mixtures of CCl_4 - CH_2I_2 and CCl_4 - C_6H_6 . The

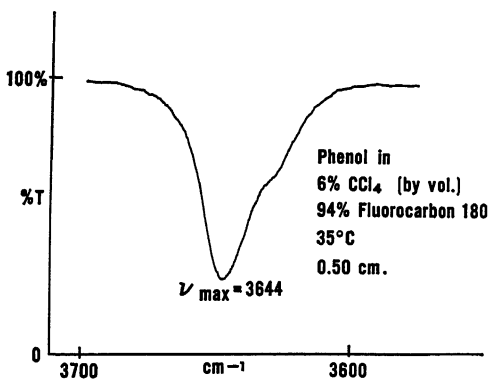


FIG. 3. Phenol solution, fundamental shows "association" of phenol to carbon tetrachloride.

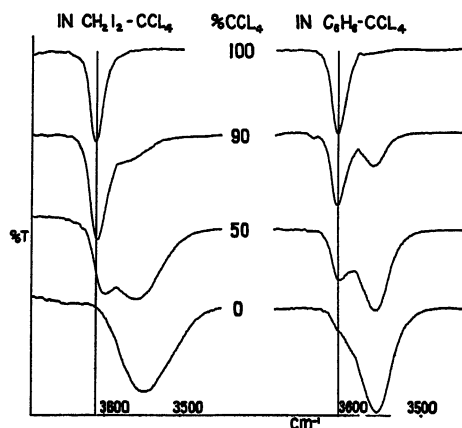


FIG. 4. Phenol solutions, fundamental comparison of "association" of phenol with methylene iodide and with benzene.

perturbations in benzene and methylene chloride are about the same yet there are significant differences in the source of the perturbation. It is very difficult to imagine a dipolar field large enough in benzene to account for the shift. However the pi electrons of the ring could form a weak hydrogen bond with the OH group. Assuming that the phenol does complex with both methylene iodide and benzene and that the area under the lower frequency band is a measure of the concentration of these complexes, one may calculate the equilibrium constant and free energy change for the reaction phenol + solvent $\rightleftharpoons$ complex. Table 4 gives the necessary data. There is some uncertainty that the usual principles of mass action can be applied here since the equilibrium constant for the stoichiometric "partitioning" of phenol between the two solvent components would be 0.092 and no complexing of any kind need be postulated. Of course it should be recognized that solubility implies some attraction. Solvents such as perfluorokerosene which show very little shift are very poor solvents for phenol. Carrying this idea further it is possible to show repulsions between dipoles when they are forced to be adjacent on the same molecule. In this case bands are shifted to higher frequencies.

Two other observations may be cited to show a distinction between the hydrogen bond and a dipolar interaction. The overtone bands of hydrogen bonded OH groups are very weak while the corresponding bands of electrostatically perturbed OH groups are of normal intensity. Also intermolecular hydrogen bonds can form between an OH group and a Lewis base as long as steric factors permit, while OH groups are intramolecularly perturbed by halogens only when steric effects force the groups into juxtaposition.

Table 5 summarizes the strengths and perturbations of three of the types of molecular interactions. Values shown here are only ranges. The coordinate band values are for one specific reaction, *n*-amyl alcohol with

TABLE 4. PHENOL SOLUTIONS

	Solvent			
	CCl ₄	C ₆ H ₆	CH ₂ I ₂	
Concentration	0.0258	0.0363	0.0395	Moles/L
A max	191	171	103	L/Mole-cm
Integrated A	3880	7570	7000	L/Mole-cm
ν max	3613	3558	3550	cm ⁻¹
$\nu\frac{1}{2}$	17	36	63	cm ⁻¹
K		0.4	0.25	
ΔF°		0.5	0.8	Kcal/Mol
ΔH		1.9	<0.5	Kcal/Mol

TABLE 5. TYPES OF MOLECULAR INTERACTIONS
R-OH FUNDAMENTALS

Type	K	ΔH	$\Delta\nu$
Dipolar	<0.3	>-0.5	<100 cm ⁻¹
H Bond	0.4 to 10	-0.5 to -5.0	100-500
Coordinate Bond (Sn Cl ₄)	7×10^8	-22	100

stannic chloride in a carbon tetrachloride solution. Other types of coordinate interactions covering a very wide range of equilibrium constants could be cited. It is significant that techniques of near infrared spectroscopy can be used to study interactions covering such a wide range of strength. Future studies of this type will certainly add much to our knowledge of solvent action, reactivity and other molecular behavior related to the term "polarity."

REFERENCES

- ADAMS, R. M. AND KATZ, J. J., "New Variable Thickness Infrared Cell and the Infrared Spectra of HF, DF, H₂O and D₂O", *J. Opt. Soc. Am.*, **46**, 895-8 (1956).
- ALLEN, H. C. JR., TIDWELL, E. D. AND PLYLER, E. K., "Infrared Spectrum of Acetylene", *J. Research N. B. S.*, **57**, 213-215 (1956).
- ALLEN, H. C. JR. AND PLYLER, E. K., " ν_3 Band of Methane", *J. Chem. Phys.*, **26**, 972-973 (1957).
- BAIN, O. AND GIGUERE, P. A., "Hydrogen Peroxide and its Analogues VI Infrared

INFRARED SPECTROPHOTOMETRY

- Spectra of H_2O_2 , D_2O_2 , and HDO_2 ", *Can. J. Chem.*, **33**, 527-545 (1955).
5. BAIN, G. H., "A Direct Infrared Method For Determining 4-Methyl 2,6-Ditertiarybutyl Phenol in Mineral Oil", *Appl. Spectroscopy*, **10**, 193-194 (1956).
6. BAKER, A. N. AND WEBBER, D. S., "Hydrogen Vibration Spectra of Rochelle Salt", *J. Chem. Phys.*, **27**, 689-692 (1957).
7. BAKER, A. W., "Hydroxyl Stretching Frequencies and Chemical Reactivities of Substituted Phenols", *J. Phys. Chem.*, **62**, 744-747 (1958).
8. BAKER, A. W. AND SHULGIN, A. T., "Intramolecular Hydrogen Bonds to π Electrons and Other Weakly Basic Groups", *J. Am. Chem. Soc.*, **80**, 5358-5363 (1958).
9. BARCELO, J. R., "The Infrared Spectrum of Some Metallic Chelate Compounds I—Rubeanate", *Spectrochim. Acta*, **10**, 245-249 (1958).
10. BARROW, G. M., "The Intensities of Infrared Hydroxyl Bands", *J. Phys. Chem.*, **59**, 1129-1132 (1955).
11. BEACHELL, H. C. AND LEVY, E. J., "Near Infrared Spectrum of Liquid Diborane", *J. Chem. Phys.*, **23**, 2168-2170 (1955).
12. BECKER, E. D. AND PIMENTEL, G. C., "Spectroscopic Studies of Reactive Molecules by the Matrix Isolation Method", *J. Chem. Phys.*, **25**, 225-228 (1956).
13. BELLAMY, L. J. AND WILLIAMS, R. L., "The NH Stretching Frequencies of Primary Amines", *Spectrochim. Acta*, **9**, 341-345 (1957).
14. BENEDICT, W. S., GAILOR, N. AND PLYLER, E. K., "Rotation-Vibration Spectra of Deuterated Water Vapor", *J. Chem. Phys.*, **24**, 1139-1165 (1956).
15. BENSON, A. M., JR. AND DRICKAMER, H. G., "Stretching Vibrations in Condensed Systems. Especially Bonds Containing Hydrogen", *J. Chem. Phys.*, **27**, 1164-1174 (1957).
16. BERNSTEIN, R. B. AND TAMRES, M., "Concentration Dependence of Solvent Shift in the C—H (and C—D) Stretching Frequencies of Chloroform and Pentachloroethane", *J. Chem. Phys.*, **23**, 2201-2202 (1955).
17. BLADES, H. AND HODGINS, J. W., "Absorption Spectra of Metals in Solution", *Can. J. Chem.*, **33**, 411-425 (1955).
18. BOVEY, L. F. H., STEERS, E. B. M. AND WISE, H. S., "The Infrared Resonance Lines of Lutetium", *Proc. Phys. Soc. A*, **69**, 783-784 (1956).
19. BOWMAN, R. S., STEVENS, D. K., AND BALDWIN, W. E., "Steric and Resonance Effects in the t-Butyl and Isobutyl Phenols", *J. Am. Chem. Soc.*, **79**, 87-92 (1957).
20. BROWN, T. L., "The Integrated Intensity of the Infrared OH Absorption in Phenols", *J. Phys. Chem.*, **61**, 820-821 (1957).
21. BROWN, R. G. AND EDWARDS, T. H., "Infrared Spectrum of Methyl Chloride near 6000 cm^{-1} ", *J. Chem. Phys.*, **28**, 384-388 (1958).
22. BROWN, T. L., SANDRI, J. M. AND HART, L., "The Intensity of Infrared OH Absorption for Some Tertiary Aliphatic Alcohols; The Inductive Properties of the Cyclopropyl Group", *J. Phys. Chem.*, **61**, 698-699 (1957).
23. BROWN, T. L. AND ROGERS, M. T., "The Integrated Intensity of the OH Stretching Band in Aliphatic Alcohols", *J. Am. Chem. Soc.*, **79**, 577-578 (1957).
24. BROWN, T. L., "The Solvent Effect in Infrared Intensities", *Spectrochim. Acta*, **10**, 149-153 (1957).
25. BUCKINGHAM, A. D., "Solvent Effects in Infrared Spectroscopy", *Proc. Roy. Soc. London*, **248**, 169-182 (1958).
26. BULANIN, M. O., "On the Struction of Absorption Bands of Liquid H_2O , D_2O and HDO . Determined by Their Molecular Structure", *Optika i Spektroskopiya*, **2**, 557-561 (1957).
27. BURCH, D. E., HOWARD, J. N., AND WILLIAMS, D., "Infrared Transmission of Synthetic Atmospheres V Absorption Laws for Overlapping Bands", *J. Opt. Soc. Am.*, **46**, 452-455 (1956).
28. BURGOVA, M. P., KUCHIREK, Y. AND PROSKURINA, L., "Anharmonicity as One of the Characteristics of Intermolecular Suteraction", *Optika i Spektroskopiya*, **5**, 141-146 (1958).
29. BUSING, W. R., "Infrared Spectra and Structure of NaOH and NaOD", *J. Chem. Phys.*, **23**, 933-936 (1955).
30. BUSING, W. R. AND MORGAN, H. W., "Infrared Spectrum of $\text{Ca}(\text{OH})_2$ ", *J. Chem. Phys.*, **28**, 998-999 (1958).
31. BYERS, F., AND SPURR, R. A., "Infrared Intensity of the S—H Stretching Vibration", *Anal. Chem.*, **27**, 321 (1955).
32. CANNON, C. G., "The Interactions and Structure of the —CONH— Group in Amides and Polyamides", *Mikrochim. Acta*, 555-588 (1955).
33. CANNON, C. G., "Infrared Frequency Shifts

- and Amide Group Interactions", *J. Chem. Phys.*, **24**, 491-492 (1956).
34. CANNON, C. G., "The Nature of Hydrogen Bonding—A Review of Published Work and Discussions", *Spectrochim. Acta*, **10**, 341-368 (1958).
 35. CANNON, C. G., "The Interaction of NH_3 and CDCl_3 Molecules in CCl_4 Solution from Infrared Spectra", *Spectrochim. Acta*, **10**, 429-430 (1958).
 36. CANNON, C. G. AND STACE, B. C., " νOH of Trifluorethanol and the Kirkwood-Bauer Relation", *Spectrochim. Acta*, **13**, 253-254 (1958).
 37. CHAPMAN, D., "A Rapid Spectroscopic Method For the Determination of Water in Glycerol", *Analyst*, **83**, 377-379 (1958).
 38. COATES, V., MILLER, T., AND SAVITZKY, A., "The Performance of the Perkin Elmer Model 21 in the Region 210 to 2000 $\text{m}\mu$ ", *Appl. Spect.*, **9**, 14-19 (1955).
 39. CORDES, H. F. AND TAIT, C. W., "Determination of Water in Several Hydrazines", *Anal. Chem.*, **29**, 485-487 (1957).
 40. COUBTOY, C. P., "Vibration-Rotation Spectra of Simple Diatomic or Polyatomic Molecules Using A Long Absorption Path XII The Spectrum of C^{13}O_2 Between 3500 and 8000 cm^{-1} and The Molecular Constants of this Molecule", *Can. J. Phys.*, **35**, 608-648 (1957).
 41. DERKSEN, W. L., MONAHAN, T. J., AND LAWES, A. J., "Automatic Recording Reflectometer for Measuring Diffuse Reflectance in the Visible and Infrared Regions", *J. Opt. Soc. Am.*, **47**, 995-999 (1957).
 42. DIAMOND, W. J., "Water Determination in Oil-Contaminated 'Freon 12' by Infrared Spectrophotometry", *Appl. Spectroscopy*, **12**, 10-11 (1958).
 43. DMITRIEVSKII, O. D., NEPORENT, V. S., AND NIKITEN, V. A., "A High Speed Infrared Spectrometer for the Region 0.8-3.0 μ ", *Optika i Spectroskopiya*, **3**, 180-181 (1957).
 44. ENS, A. AND MURRAY, F. E., "A Quantitative Infrared Spectrometric Study of Molecular Association in Alcohols", *Can. J. Chem.*, **35**, 170 (1957).
 45. FINCH, J. N. AND LIPPINCOTT, E. R., "Hydrogen Bond Systems: Temperature Dependence of OH Frequency Shifts and OH Band Intensities", *J. Chem. Phys.*, **24**, 908-909 (1956).
 46. FINCH, J. N. AND LIPPINCOTT, E. R., "Hydrogen Bond Systems—Temperature Dependence of OH Frequency Shifts and OH Band Intensities", *J. Phys. Chem.*, **61**, 894-902 (1957).
 47. FISHMAN, E. AND DRICKAMEN, H. G., "Effect of Pressure on the Frequency of the OH Band in Butanol Solutions", *J. Chem. Phys.*, **24**, 548-553 (1956).
 48. FLETT, M. Sr. C., "Studies of the Band Near 3 μ in Some Hydroxyl Compounds", *Spectrochim. Acta*, **10**, 21-37 (1957).
 49. FORD, M. A., PRICE, W. C., AND WILKINSON, T. R., "A High Resolution Grating Spectrometer for the Infrared Region", *J. Sci. Inst.*, **35**, 55-58 (1958).
 50. FRANCE, W. L. AND DICKEY, F. P., "Fine Structure of the 2.7 Micon CO_2 Rotation-Vibration Band," *J. Chem. Phys.*, **23**, 471-474 (1955).
 51. FRASER, R. D. B., "Interpretation of J. R. Dichroism in Fibrous Proteins—the 2 μ Region," *J. Chem. Phys.*, **24**, 89-95 (1956).
 52. FREEMAN, S. K., "Infrared Spectrophotometric Determination of Allethrin," *Anal. Chem.*, **27**, 1268-1274 (1955).
 53. FUSON, N., PINEAU, P., AND JOSIEN, M. L., "Determination by Infrared Spectroscopy of Associations Constants of Proton 'donors'—'Acceptors' complexes I Complexes joined between pyrrole or phenol and some proton Acceptors," *J. Chem. Phys.*, **55**, 454-463 (1958).
 54. GARINO-CANINA, V., "Contributions to the Knowledge of Fused Silica," *Cahiers d. Phys.*, **66**, 43-57 (1956).
 55. GATES, D. M., MURCHAY, D. G., SHAW, C. C., AND HERBOLD, R. J., "Near IR Solar Radiation Measurements by Balloon to an Altitude of 100,000 Feet," *J. Opt. Soc. Am.*, **48**, 1010-1016 (1958).
 56. GAUNT, J., "The Analysis of Heavy Water by Infrared Spectrometry," *Spectrochim. Acta*, **8**, 57-65 (1956).
 57. GODDU, R. F., "Determination of Unsaturation by Near Infrared Spectrophotometry," *Anal. Chem.*, **29**, 1790-1794 (1957).
 58. GODDU, R. F., "Determination of Phenolic Hydroxyl by Near Infrared Spectrophotometry," *Anal. Chem.*, **30**, 2009-2013 (1958).
 59. GODDU, R. F. AND DELKER, D. A., "Determination of Terminal Epoxides by Near Infrared Spectrophotometry," *Anal. Chem.*, **30**, 2013-2016 (1958).
 60. GRENIER-BESSON, M. L., "Contributions to the Study of the Vibration-Rotation Spectrum of N_2O ," *Cahiers d. Phys.*, **69**, 44-84 (1956).
 61. GROENWEGE, M. P. AND VAN VUCHT, H. A.,

- "Analytical Applications of the Near Infrared Using the Beckman UV Spectrophotometer," *Mikrochemie ver. Mikrochim-Acta*, 471-480 (1955).
62. GREINACHER, E., LÜTTKE, W., AND MECKE, R., "Infrared Spectroscopy of Water in Organic Solvents," *Z. Elektrochem.*, **59**, 23-31 (1955).
 63. HAAS, C. AND KETELAAR, J. A. A., "The Effective Field and the Frequency of Overtones and Combination Bands in the Vibration Spectra of Crystals," *Physica*, **22**, 1286-1290 (1956).
 64. HÄUSLER, C., "Measurement of the Ammonia Band at 1.98μ ," *C.R.*, **240**, 507-508 (1955).
 65. HARKINS, T. R., WALTER, J. L., HARRIS, O. E., AND FREISER, H., "An Infrared Study of the Metal Chelates of Some Imidazole Derivatives," *J. Am. Chem. Soc.*, **78**, 260-264 (1956).
 66. HEAVENS, O. S., KING, J., AND SMITH, S. D., "Interference Filters for the Infrared," *Spectrochim. Acta*, **10**, 179-194 (1957).
 67. HEDIGER, H. J. AND GUNTARD, H. H., "Optical Rotatory Power of Organic Substances in the Infrared Region," *Helv. Chim. Acta*, **37**, 1125-1133 (1954).
 68. HEXTER, R. M., "On the Infrared Absorption Spectra Crystalline Brucite $Mg(OH)_2$ and Portlandite $Ca(OH)_2$," *J. Opt. Soc. Am.*, **48**, 770-774 (1958).
 69. HEXTER, R. M., "High Resolution Temperature Dependent Spectra of Calcite," *Spectrochim. Acta*, **10**, 281-290 (1958).
 70. HEXTER, R. M., "Infrared Spectroscopic Investigations of Anion Rotational Disorder in Sodium Nitrate," *Spectrochim. Acta*, **10**, 291-298 (1958).
 71. HOFFMAN, K. H. AND FISCHER, L., "Determination of Small Amounts of Water in Films and Organic Liquids," *Chemica Ing. Tech.*, **10**, 604-607 (1955).
 72. HOLMAN, R. T. AND EDMONDSON, P. R., "Near Infrared Spectra of Fatty Acids and Some Related Substances," *Anal. Chem.*, **28**, 1533-1538 (1956).
 73. VAN HORNE, B. H. AND HARRIS, C. D., "Near Infrared Spectrum of DCl ," *J. Chem. Phys.*, **25**, 56-59 (1956).
 74. HUGGINS, C. M. AND PIMENTEL, G. C., "Systematics of the Infrared Spectra Properties of Hydrogen Bonding Systems: Frequency Shift Half Width and Intensity," *J. Phys. Chem.*, **60**, 1615-1619 (1956).
 75. HUGHES, R. H., MARTIN, R. J., AND COGGESHALL, M. D., "Temperature Dependence of Infrared Absorptions," *J. Chem. Phys.*, **24**, 489-490 (1956).
 76. INGRAHAM, L. L., CORSE, J., BAILEY, G. F., AND STITT, F., "Correlation of OH Stretching Frequencies in Phenols and Catachols with Chemical Reactivities," *J. Am. Chem. Soc.*, **74**, 2297-2299 (1952).
 77. INSKEEP, R. G., KELLIKER, J. M., MCMAHON, P. E., AND SOMERS, B. J., "Molecular Association of Methanol Vapor," *J. Chem. Phys.*, **28**, 1033-1038 (1958).
 78. JACQUEZ, J. A., MCKEEHAN, W., HUSS, J., DMITROFF, J. M., AND KUPPENHEIM, H. F., "Integration Sphere for Measuring Diffuse Reflectance in the Near Infrared," *J. Opt. Soc. Am.*, **45**, 781-784 (1955).
 79. JAFFE, J. H., RANK, D. H., AND WIGGINS, T. A., "High Resolution in the Infrared by Interferometry Unambiguous Display Without Overlapping Orders," *J. Opt. Soc. Am.*, **45**, 636-643 (1955).
 80. JAFFE, J. H. AND KIMEL, S., "Infrared Intensities in Liquids," *J. Chem. Phys.*, **25**, 374-375 (1956).
 81. JAFFE, J. H., HIRSCHFELD, N. A., AND KIMEL, S., "Optical Dispersion of Gases in the Infrared," *J. Chem. Phys.*, **29**, 675-676 (1958).
 82. JOSIEN, M. L. AND SOURISSEAU, G., "The Infrared Spectrum of Hydrochloric Acid in Solution, Formation of Organic Complexes," *Bull. Soc. Chim.*, 178-183 (1955).
 83. JOSIEN, M. L., SOURISSEAU, G., AND CASTINEL, C., "Infrared Spectra of Hydrobromic and Hydroiodic Acids in Soln. Formation or Organic Complexes," *Bull. Soc. Chim.*, 1539 (1955).
 84. JOSIEN, M. D. AND SAUMAGNE, P., "Infrared Spectrum in the 2500 cm^{-1} region of Hydrogen Sulfide Solutions. Formation of Molecular Complexes," *Bull. Soc. Chim. France*, 937-941 (1956).
 85. JOSIEN, M. L. AND DIZABO, P., "Formation of Molecular Complexes with Pyrrole, Benzenethiol, Phenol the alcohols and the Monohalogenated Alkanes," *Compt. Rend.*, **243**, 44-46 (1956).
 86. JOSIEN, M. L., LASCOMBE, J., AND FUSEN, N., "Effect of Pressure on the OH Stretching Frequency of Butanol in nonpolar Solvents," *J. Chem. Phys.*, **25**, 1291-1292 (1956).
 87. JOSIEN, M. L., CASTINEL, C., AND SAUMAGNE, P., "Determination of Infrared Spectroscopy of Hydrogen Bands formed by the SH Vibrator II. The monohalogen benzene-

- thiols," *Bull. Soc. Chim. France*, 648-650 (1957).
88. KAGARISE, R. E., "Infrared Intensity of the C—H Stretching Band of Chloroform in Some Halogenated Acetones," *J. Chem. Phys.*, **27**, 827-828 (1957).
 89. KAYLOR, H. M. AND NIELSEN, A. H., "Infrared Spectrum and Molecular Constants of CD_4 ," *J. Chem. Phys.*, **23**, 2139-2152 (1955).
 90. KOGON, I. C., "Evidence for Intramolecular Hydrogen Bonding in Aryl Allophanates and Alkyl or Aryl-Alkyl Biurets," *J. Am. Chem. Soc.*, **79**, 2253-2254 (1957).
 91. KUIPERS, G. A., "The Spectrum of Monomeric Hydrogen Fluoride Line Shapes, Intensities, and Breadths," *J. Mol. Spect.*, **2**, 75-98 (1958).
 92. LACHER, J. R., BITNER, J. L., AND PARK, J. D., "The Infrared Absorption Spectra of Some Antibiotics in Antimony Trichloride Solution," *J. Phys. Chem.*, **59**, 610-614 (1955).
 93. LACHER, J. R., BITNER, J. L., EMERY, D. J., SEFFL, M. E., AND PARK, L. D., "The Infrared Absorption Spectra, Some Substituted Purines and Pyrimidenes in Antimony Trichloride Solutions," *J. Phys. Chem.*, **59**, 615-625 (1955).
 94. LAGERGIST, A., AND HULT, L., "Flame Spectra of Metal Compounds in the Infrared," *Ark. Fys.*, **12**, 491-494 (1957).
 95. LASCOMBE, J., SOURISSEAU, G., SAUMAGNE, P., CASTINEL, C., DIZABO, P., LEICKMAN, J. P., AND JOSSEN, M. L., Application of the Theory of Kirkwood—Bauer—Magat to the Detection of Molecular Association, *Cahiers de Phys.*—No. 73, 44-46 (1956).
 96. LIDDEL, U. AND BECKER, E. D., "Infrared Spectroscopic Studies of Hydrogen Bonding in Methanol, Ethanol & t-Butanol," *Spectrochim. Acta*, **10**, 70-84 (1957).
 97. LINDQUIST, J., "Studies on Arsenic Trichloride as a Solvent. II the Constitution of Solns of $AsCl_3$," *Acta. Chem. Scand.*, **9**, 73-78 (1955).
 98. LUCCHESI, P., "Infrared Study of the Acetone-Water System," *J. Am. Chem. Soc.*, **78**, 4229-4230 (1956).
 99. MALCOLM, B. R., "The Mounting of Fibres and Organic Crystals for Spectroscopy in the Near Infrared Region," *J. Sci. Inst.*, **35**, 423 (1958).
 100. MARA, R. T. AND SUTHERLAND, G. B. B. M., "Crystal Structure of Brucite and Portlandite in Relation to Infrared Absorption," *J. Opt. Soc. Am.*, **46**, 464 (1956).
 101. McALLISTER, E. D., VILLA, J. J., AND SALZBERG, C. D., "Rapid and Accurate Measurement of Refractive Index in the Infrared," *J. Opt. Soc. Am.*, **46**, 485-487 (1956).
 102. McDONALD, R. S., GIBBS, J. H., AND LADD, J. R., "Absence of Hydrogen Bonding in an Alcohol-Fluorohydrocarbon System," *J. Chem. Phys.*, **23**, 1170 (1955).
 103. McDONALD, R. S., "Study of the Interaction Between Hydroxyl Groups of Aerosil Silica and Adsorbed Non-Polar Molecules by I.R. Spectrometry," *J. Am. Chem. Soc.*, **79**, 850-854 (1957).
 104. McDONALD, R. S., "Surface Functionality of Amorphous Silica by Infrared Spectroscopy," *J. Phys. Chem.*, **62**, 1169-1178 (1958).
 105. MENEFEE, A., ALFORD, D., AND SCOTT, C. B., "Hydrogen Bonding of the Thiol Group," *J. Chem. Phys.*, **25**, 370-371 (1956).
 106. METZ, C. F., "The Analytical Chemistry of Plutonium," *Anal. Chem.*, **29**, 1748-1756 (1957).
 107. MITCHELL, E. W. J. AND RIGDEN, J. D., "The Effects of Radiation on the Near Infrared Absorption Spectra of α -Quartz," *Phil. Mag.*, **2**, 941-956 (1957).
 108. MITCHELL, J. A., BOOKEMAN, C. D., AND LEE, A. V., "Determination of Acetyl Content of Cellulose Acetate by Near Infrared Spectroscopy," *Anal. Chem.*, **29**, 499-502 (1957).
 109. MIZUSHIMA, S., TSUBOI, M., SHIMANOCHI, T., AND TSUDA, Y., "Spectroscopic Investigation of the Strength of Hydrogen Bonds Formed by Amides," *Spect. Acta*, **7**, 100-107 (1955).
 110. MIZUSHIMA, S. J., SHIMANOCHI, T., TSUBOI, M., AND ARAKAWA, T., "Near Infrared Spectra of Compounds with Two Peptide Bonds and the Confirmation of a Polypeptide Chain VI Further Evidence of the Internal Hydrogen Bonding and an Estimation of its Energy," *J. Am. Chem. Soc.*, **79**, 5357-5361 (1957).
 111. MOORE, G. E., "The Spectrum of Nitrogen Dioxide in the 1.4-3.4 μ Region and the Vibrational and Rotational Constants of the NO Molecule," *J. Opt. Soc. Am.*, **43**, 1045-1050 (1955).
 112. MUKHERJEE, L. M., AND GRUNWALD, E., "Physical Properties and Hydrogen Bonding in the System Ethanol-222 Trifluoroethanol," *J. Phys. Chem.*, **62**, 1311-1314 (1958).
 113. NEPOMENT, B. S., "Vacuum Grating Spectrometer for the 0.7 to 3 μ Region," *Optika i Spektrosk.*, **3**, 289-293 (1957).
 114. NICHOLS, N. L., HAUSE, C. D., AND NOBLE,

INFRARED SPECTROPHOTOMETRY

- R. H., "Near Infrared Spectrum of Nitric Oxide," *J. Chem. Phys.*, **23**, 57-61 (1955).
115. PARSONS, J. L., IRELAND, M. J., AND BRYAN, F. R., "Continuous Flow Infrared Gas Analyzer Employing Interference Filters," *J. Opt. Soc. Am.*, **46**, 164-166 (1956).
116. PEARSON, C. A. AND BOETTNER, E. A., "Horizontal Atmospheric Transmittance Measurements with a Thallous Sulfide Cell Transmissometer," *J. Opt. Soc. Am.*, **46**, 54-59 (1956).
117. PHILLIPS, B. A. AND BUSING, W. R., "Comparison of the Infrared and Raman Spectra of Some Crystalline Hydroxides," *J. Phys. Chem.*, **61**, 502 (1957).
118. PINCHAS, S., "Infrared Absorption of the Aldehyde C-H Group," *Anal. Chem.*, **27**, 2-6 (1955).
119. PINEAU, P., FUSON, N., AND JOSIEN, M. L., "Determination by Infrared Spectroscopy of Association Constants of Proton 'Donor-Acceptor' Complexes II General Method," *J. Chim. Phys.*, **55**, 464-469 (1958).
120. VON PLANTA, P. C., "Experimental Study of the Slit Functions of an Ebert Spectrometer in the Visible and Near Infrared," *J. Opt. Soc. Am.*, **47**, 629-631 (1957).
121. PLISKIN, W. A. AND EISCHEUS, R. P., "Infrared Spectra of Chemisorbed Olefins and Acetylene," *J. Chem. Phys.*, **24**, 482-483 (1956).
122. PLYLER, E. K., BLAINE, L. R., AND TIDWELL, E. D., "Precise Measurement of Wavelengths in IR Spectra," *J. Research N.B.S.*, **55**, 279-284 (1955).
123. PLYLER, E. K., TIDWELL, E. D., AND ALLEN, H. C., JR., "Near Infrared Spectrum of Nitrous Oxide," *J. Chem. Phys.*, **24**, 95-97 (1956).
124. PONDY, P. R. AND BEACHELL, H. C., "Near Infrared Spectra of Diborane Pentaborane, and Decaborane," *J. Chem. Phys.*, **25**, 238-241 (1956).
125. RANK, D. H., WIGGINS, T. A., GUENTHER, A. H., AND SHEARER, J. R., "Changes of Rotational Constants in some II- σ Bands of HCN and N₂O," *J. Opt. Soc. Am.*, **46**, 953-956 (1956).
126. RANK, D. H., BENNETT, J. M., AND BENNETT, H. E., "Measurement of Interferometric Secondary Wavelength Standards in the Near Infrared," *J. Opt. Soc. Am.*, **46**, 477-484 (1956).
127. RANK, D. H., GUENTHER, A. H., SHEARER, J. N., AND WIGGINS, T. A., "Secondary and Tertiary Interferometric Wavelength Standards in the 1.5-2.5 μ Region," *J. Opt. Soc. Am.*, **47**, 144-148 (1957).
128. SAKAYANAGI, Y. AND SATO, Y., "A Near Infrared Spectrometer Using A Plane Grating," *Science of Light (Tokyo)*, **3**, 84-89 (1955).
129. SAVAGE, C. M. AND EDWARD, T. H., "Infrared Spectrum of Hydrogen Sulfide in the 2.6 μ Region," *J. Chem. Phys.*, **27**, 179-181 (1957).
130. SCHLUETER, D. J. AND PECK, E. R., "Refractivity of Air in the Near Infrared," *J. Opt. Soc. Am.*, **48**, 313-315 (1958).
131. SERRATOSA, J. M. AND BRADLEY, W. F., "Determination of the Orientation of OH Bond Axes in Layer Silicates by Infrared Absorption," *J. Phys. Chem.*, **62**, 1164-1167 (1958).
132. SHIELDS, J. H. AND ELLIS, J. W., "Dispersion of Birefringence of Quartz in the Near Infrared," *J. Opt. Soc. Am.*, **46**, 263-265 (1956).
133. SKJOLDEBRAND, R., "An Infrared Spectrophotometer and its use for the Isotopic Analysis of Heavy Water," *Appl. Sci. Res.*, **B5**, 401-408 (1956).
134. SMITH, D. F., "Infrared Spectra Analysis for Hydrogen Fluoride," *Spect. Acta*, **12**, 224-232 (1958).
135. STAATS, P. A., MORGAN, H. W., AND GOLDSTEIN, J. H., "Infrared Spectra of T₂O, THO, TDO," *J. Chem. Phys.*, **24**, 917-918 (1956).
136. STONE, P. J. AND THOMPSON, H. W., "Vibrational Band Intensity of the Hydroxyl Group in Phenols," *Spect. Acta*, **10**, 17-20 (1957).
137. TALLENT, W. H. AND SIEWERS, J. J., "Carbon Hydrogen Stretching Bands in High Resolution Infrared Spectra of Heterocyclic Compounds," *Anal. Chem.*, **28**, 953-956 (1956).
138. TERENIN, A. N., JAROSLAVSKY, N. G., KARAJAKIN, A. W., AND SIDOROVA, A. I., "Infrared Spectroscopy of Molecules Absorbed on Porous Earths," *Mikrochem. Ver. Mikrochim. Acta*, 467-470 (1955).
139. THIEL, M. V., BECKER, E. D., AND PIMENTAL, G., "Infrared Studies of Hydrogen Bond of Water by the Matrix Isolation Technique," *J. Chem. Phys.*, **27**, 486-490 (1957).
140. THIEL, M. V., BECKER, E. D., AND PIMENTEL, G. C., "Infrared Studies of Hydrogen Bonding of Methanol by the Matrix Isolation Technique," *J. Chem. Phys.*, **27**, 95-99 (1957).
141. TRIFAN, D. S., WEINMANN, J. L., AND KUHN, L. P., "Intramolecular Aromatic Ring-

- Hydrogen Bonding," *J. Am. Chem. Soc.*, **79**, 6566-6567 (1958).
142. TSUBOMURA, H., "Nature of the Hydrogen Bond II. The Effect of Hydrogen Bonding and Other Solute-Solvent Interactions Upon the Shape and Intensity of the Infrared OH Band of Phenol," *J. Chem. Phys.*, **23**, 2130-2133 (1955).
 143. TSUBOMURA, H., "Nature of the Hydrogen Bond III The Measurement of the Infrared Absorption Intensities of Free and Hydrogen Bonded OH Bands. Theory of the Increase of the Intensity Due to the Hydrogen Bond," *J. Chem. Phys.*, **24**, 927-931 (1956).
 144. WAGGENER, W. C., "Absorbance of Liquid Water and Deuterium Oxide between 0.6 and 1.8 Microns-Comparison of Absorbance and Effect of Temp.," *Anal. Chem.*, **30**, 1569-1570 (1958).
 145. WALDRON, R. D., "Infrared Spectra of HDO in Water and Ionic Solutions," *J. Chem. Phys.*, **26**, 809-814 (1957).
 146. WASHBURN, W. H. AND MAHONEY, M. J., "Near Infrared Spectra with Sodium Chloride Optics," *Appl. Spect.*, **12**, 127-128 (1958).
 147. WENOGRA, J. AND SPURR, R. A., "Characteristic Integrated Intensities of Bands in the IR Spectra of Carboxylic Acids," *J. Am. Chem. Soc.*, **79**, 5844-5848 (1957).
 148. WHETSEL, K., ROBERSON, W. E., AND KRELL, M. W., "Near Infrared Analysis of N-Alkyl and N-Alkyl-N Hydroxyl Alkyl Aromatic Amine Mixtures," *Anal. Chem.*, **29**, 1006-1009 (1957).
 149. WHETSEL, K., ROBERSON, W. E., AND KRELL, M. W., "Near Infrared Analysis of Mixtures of Primary and Secondary Aromatic Amines," *Anal. Chem.*, **30**, 1594-1597 (1958).
 150. WHETSEL, K. B., ROBERSON, W. E., AND KRELL, M. W., "Near Infrared Spectra of Primary Aromatic Amines," *Anal. Chem.*, **30**, 1598-1604 (1958).
 151. WHITE, L., JR. AND BARRETT, W. J., "Determination of Water in Fuming Nitric Acid by Near Infrared Absorption," *Anal. Chem.*, **28**, 1538-1542 (1956).
 152. WIDOM, J. M., PHILIPPE, R. J., AND HOBBS, M. E., "A Study of the Association of Phenol with Several Ketones by IR Abs. Measurements," *J. Am. Chem. Soc.*, **79**, 1383-1386 (1957).
 153. WILKINSON, G. R., FORD, M. A., AND PRICE, W. C., "The Emission Spectra of Molecules and Radicals in the Infrared," *Anal. Chem.*, **27**, 162 (1955).
 154. WOOD, D. L., "Infrared Absorption Bands in d Quartz," *J. Chem. Phys.*, **27**, 1438-1439 (1957).

WILBUR I. KAYE

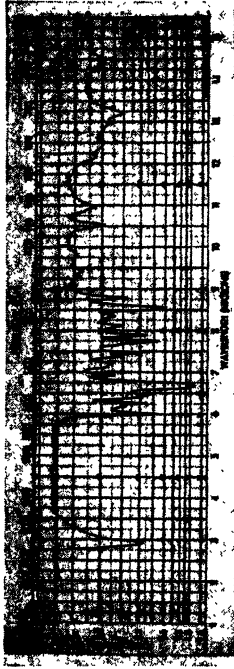
PAINT PRODUCTS

Paint consists of pigments, binders, solvents and minor components, here called additives. Since almost all of these paint ingredients exhibit characteristic infrared absorption properties, they are conveniently identified from their infrared spectra. The purpose of this section is to present a compilation of spectra which will help to illustrate the usefulness of the infrared technique as a qualitative tool for paint analysis. The spectra of typical pigments, binders, solvents, and additives are reproduced in Fig. 1. The samples represented are summarized in Tables 1 through 5.

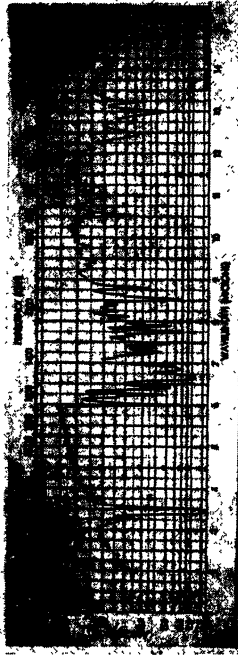
This presentation is limited to the rock salt region, the infrared region from two to fifteen microns wavelength. All of the spectra were prepared with a Perkin-Elmer Model 21 Infrared Spectrophotometer equipped with a sodium chloride prism. A programmed slit setting of "Resolution 927" and a wavelength-drive speed of about one minute per micron were used. All of the materials examined are of commercial quality. Since most of the materials are available from a number of suppliers, the source of each sample is not given. Many of the solid samples were prepared as $\frac{1}{2}$ " diameter $\frac{1}{2}$ gram KBr discs. The only absorption bands exhibited by the disc alone are those at 2.9 and 6.1 microns due to adsorbed moisture. A few samples were prepared as mineral oil mulls which have bands at 3.45, 3.50, 6.85, 7.27, and 13.9 microns due to the mineral oil. Where materials are known to give different spectra by the KBr and oil mull method, both spectra are shown.

Pigments. Pigments are generally classified as hiding and non-hiding or extender pigments. In addition they are sometimes classified according to color or according to

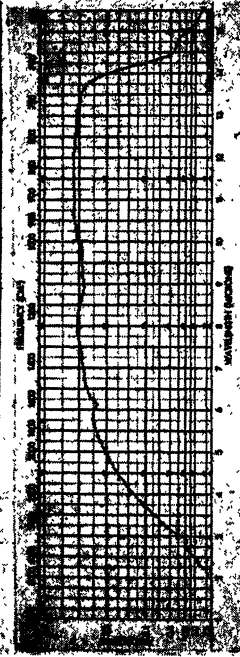
(text continued on p. 518)



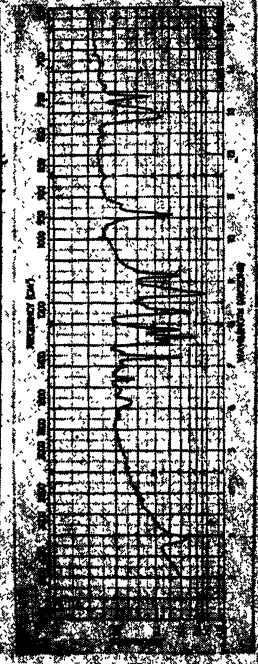
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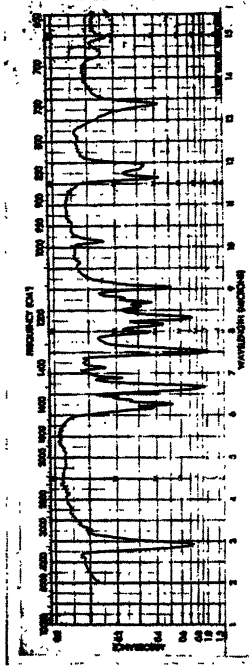


33.

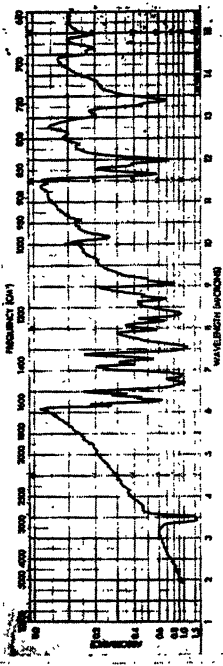


34.

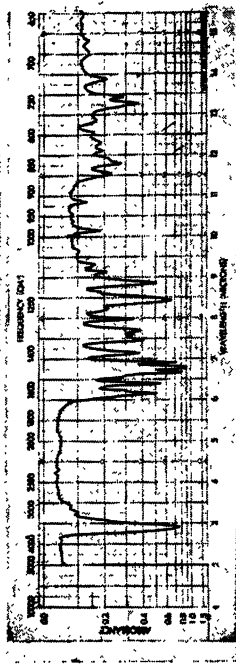
35.



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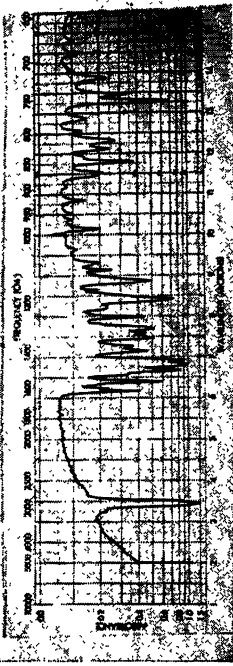
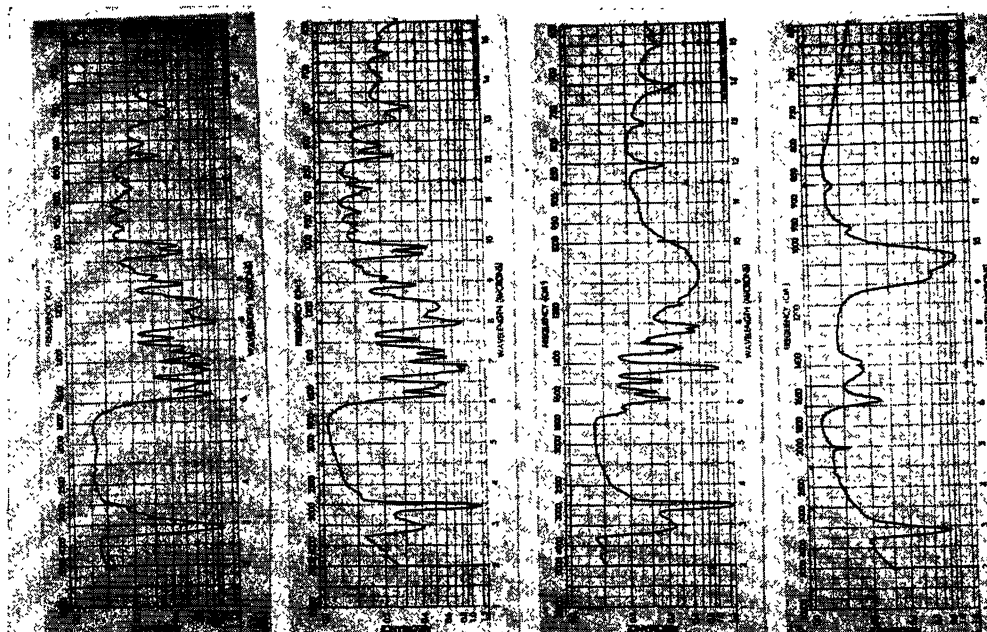


Fig. 1a



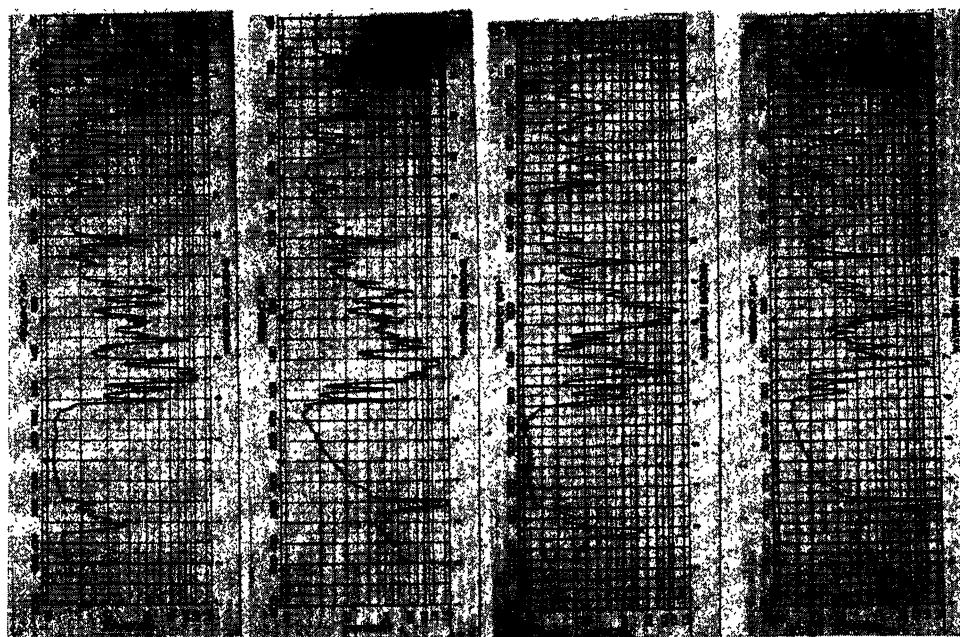
43.

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Fig. 1a. Cont'd

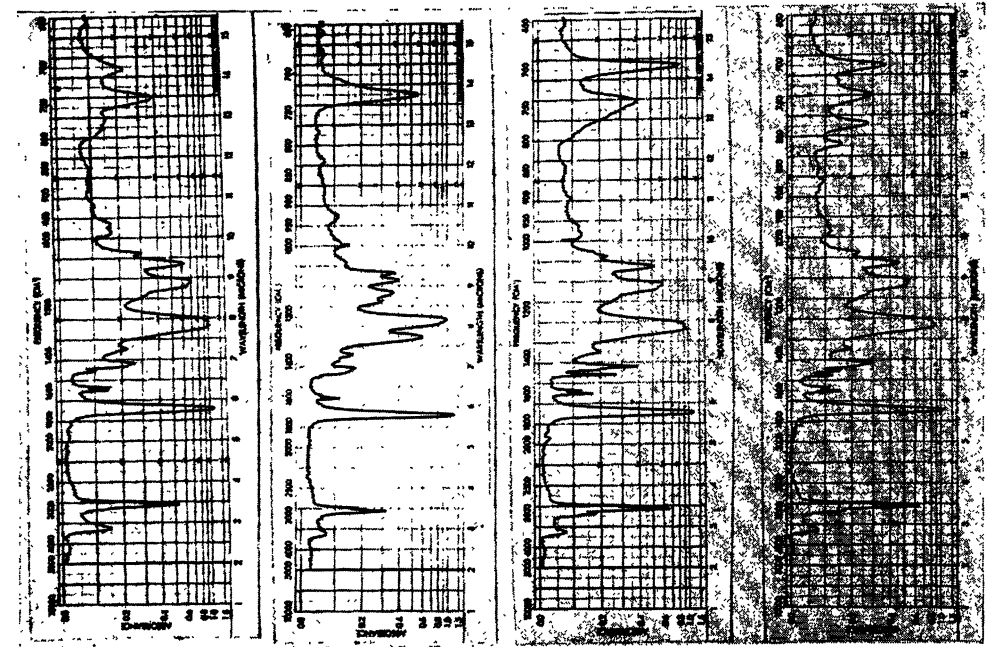


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41.

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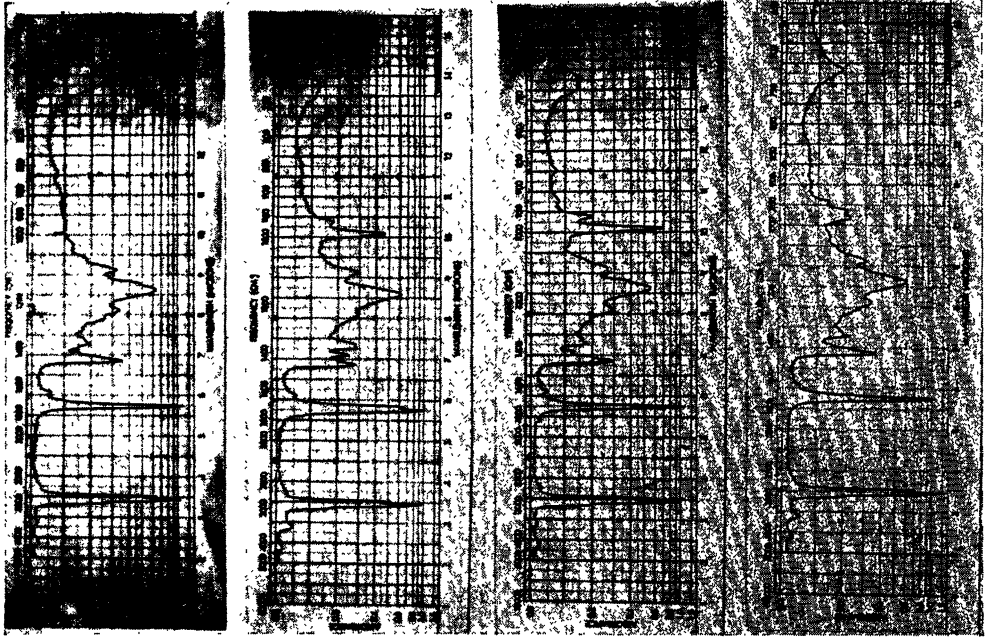
51.

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Fig. 1b



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50.

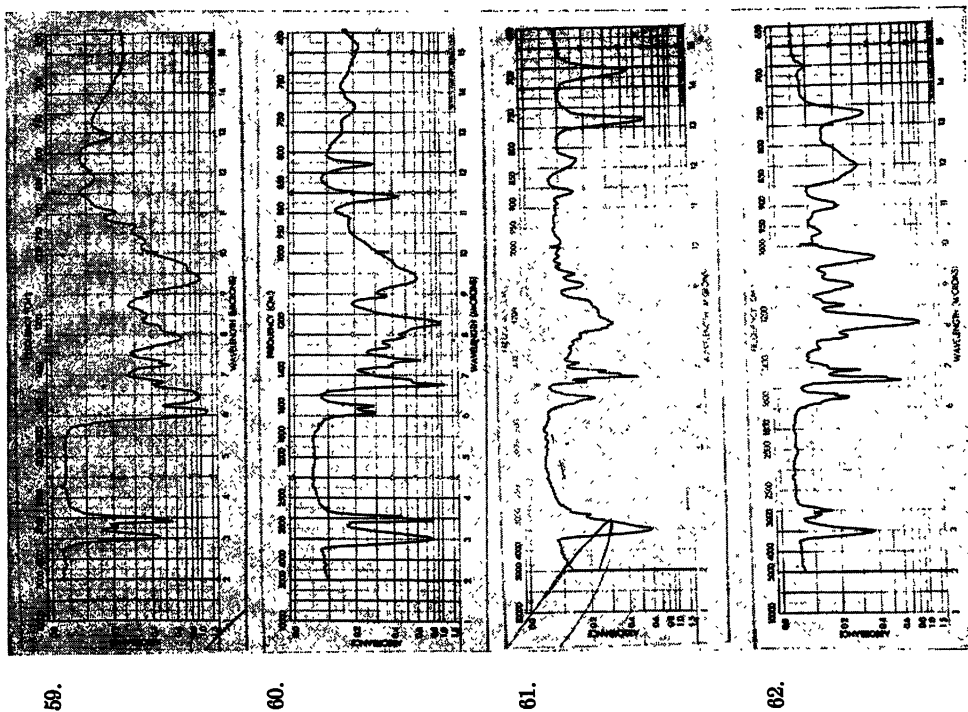
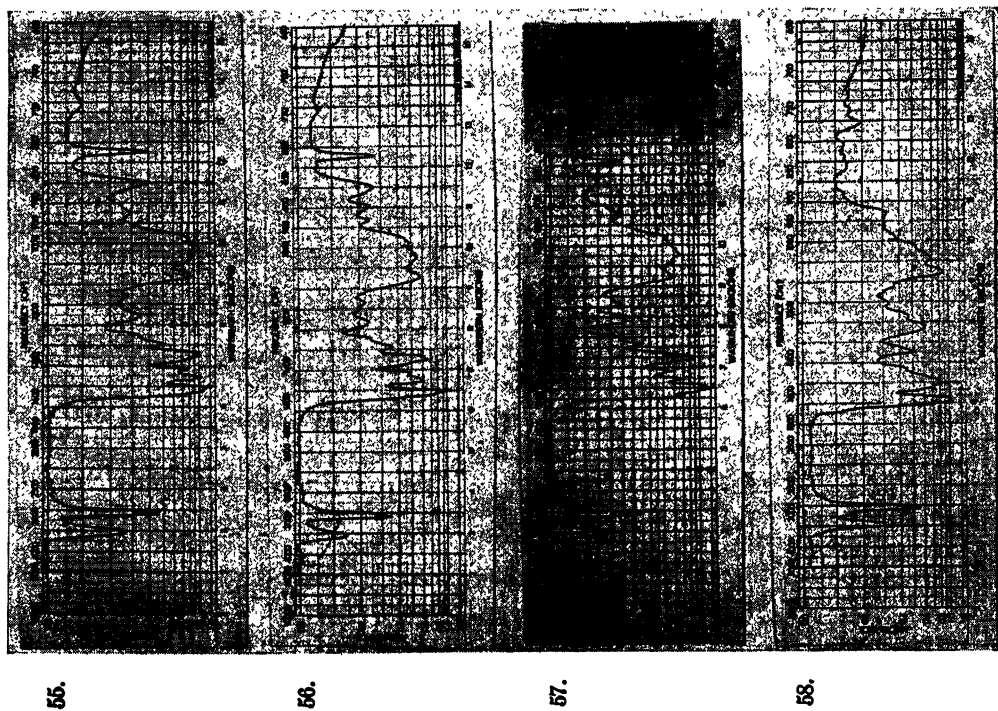
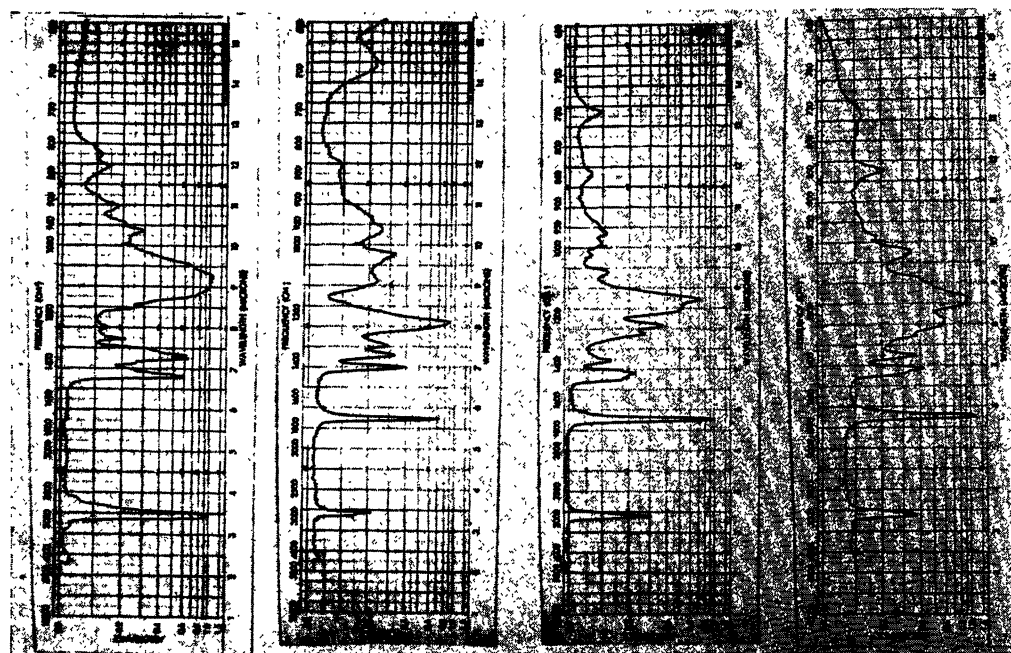


Fig. 1b. Cont'd.



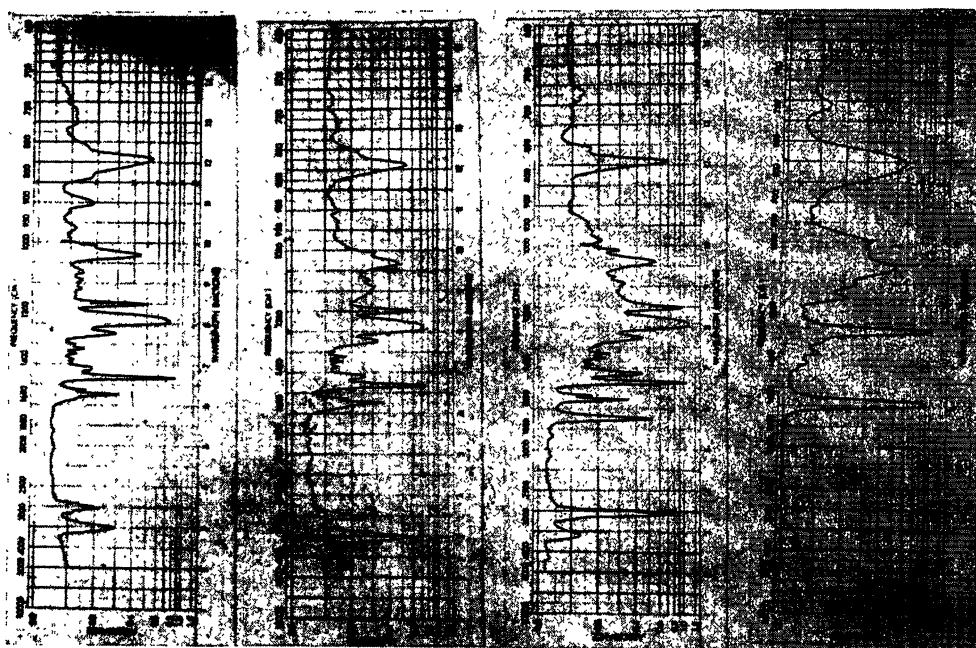
67.

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Fig. 1c



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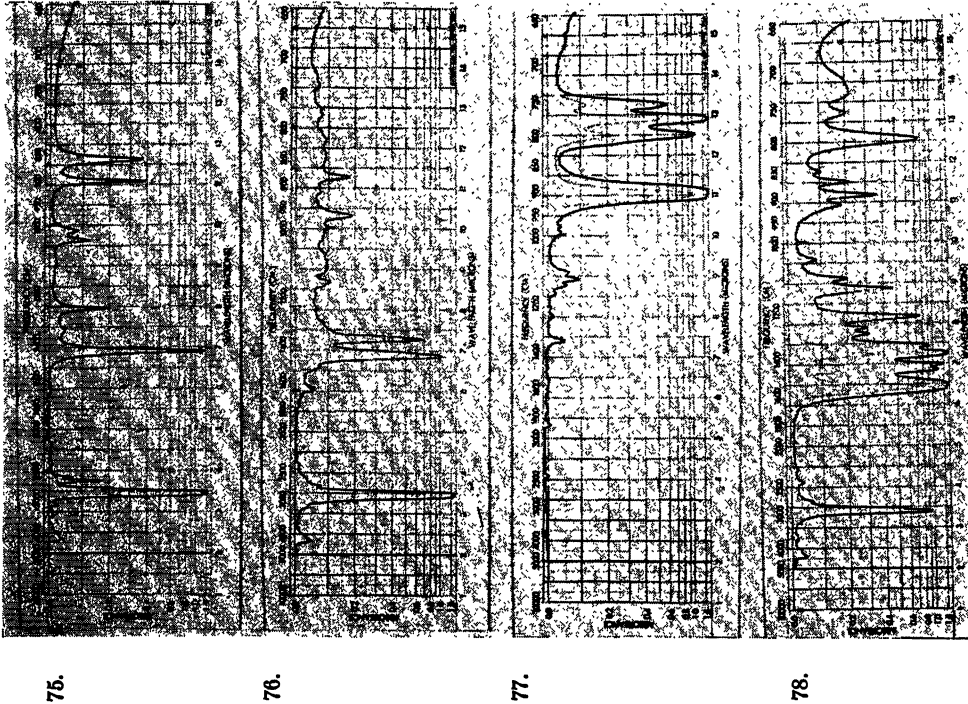
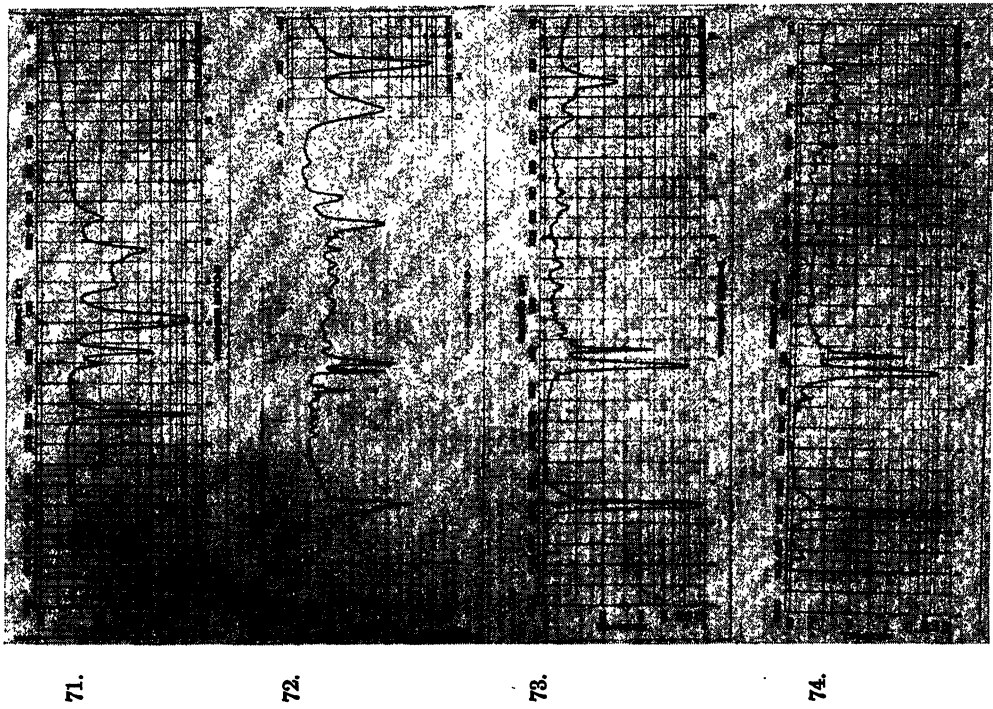
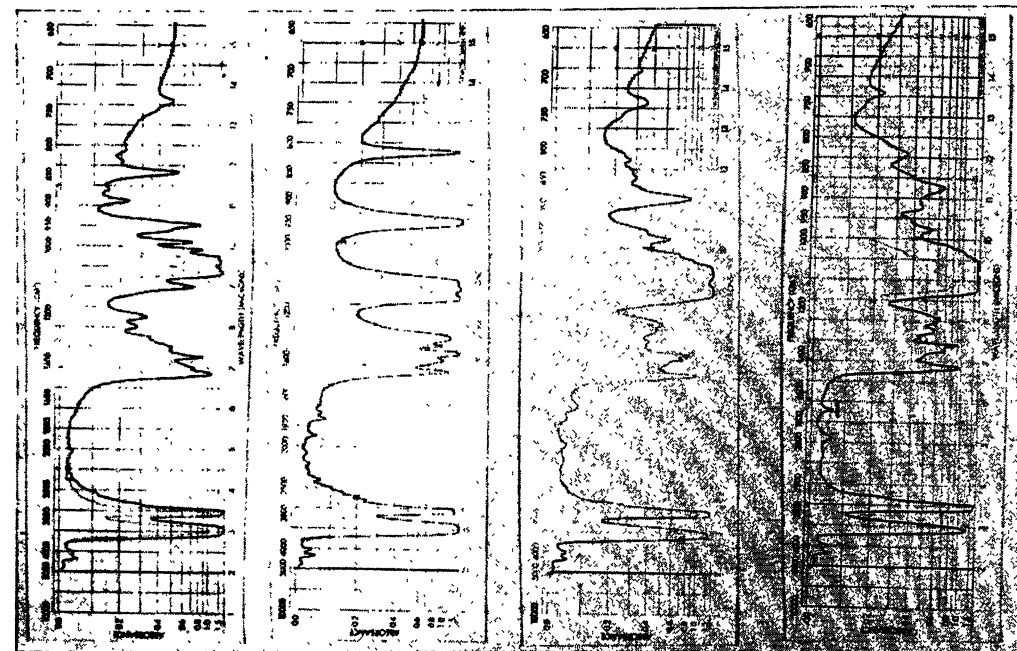


FIG. 1c. Cont'd.



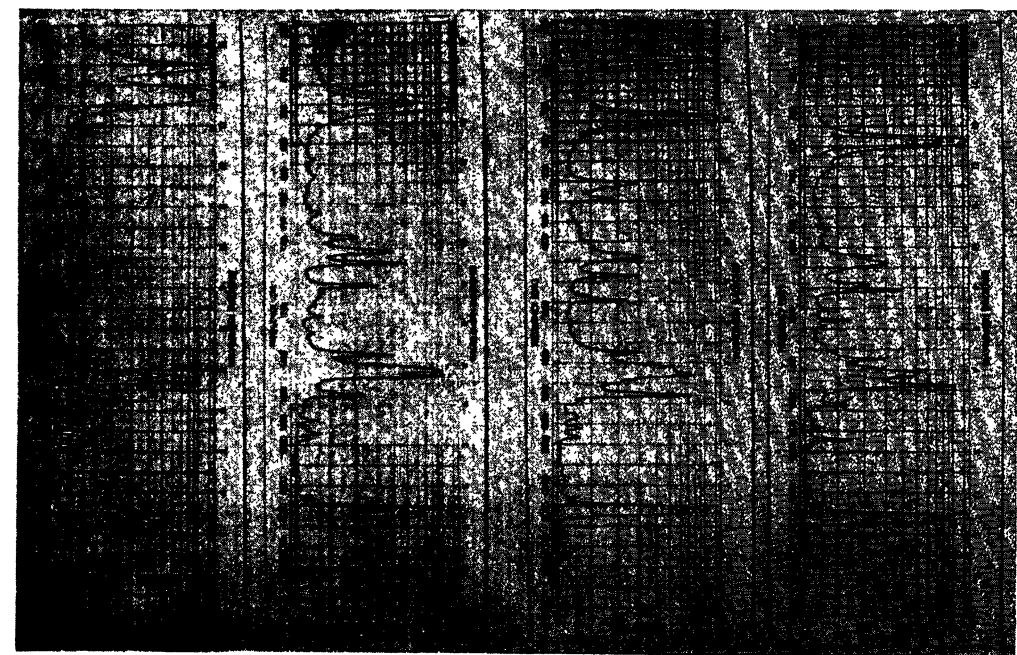
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Fig. 1d

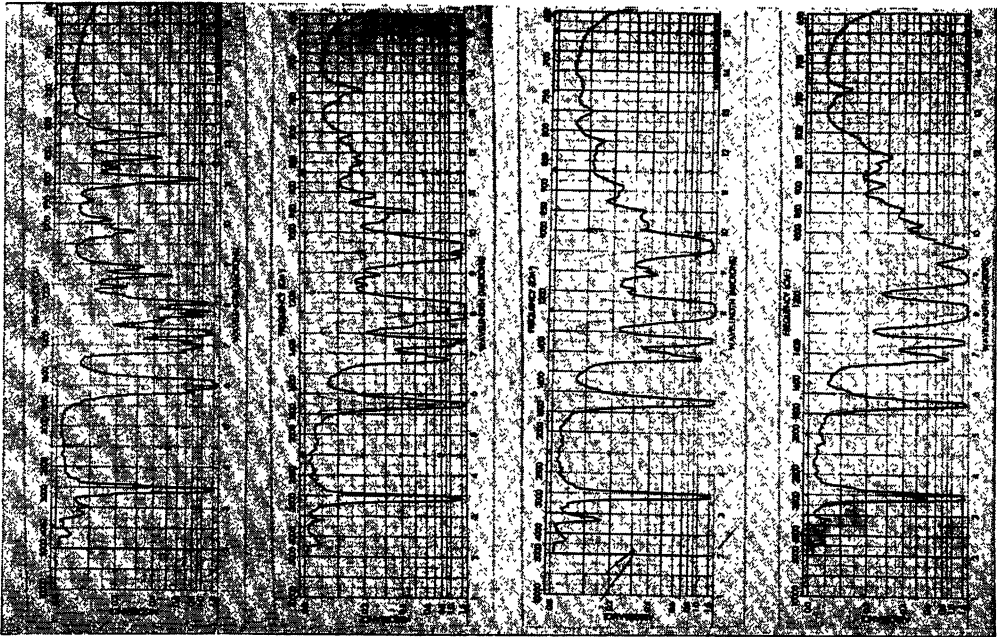


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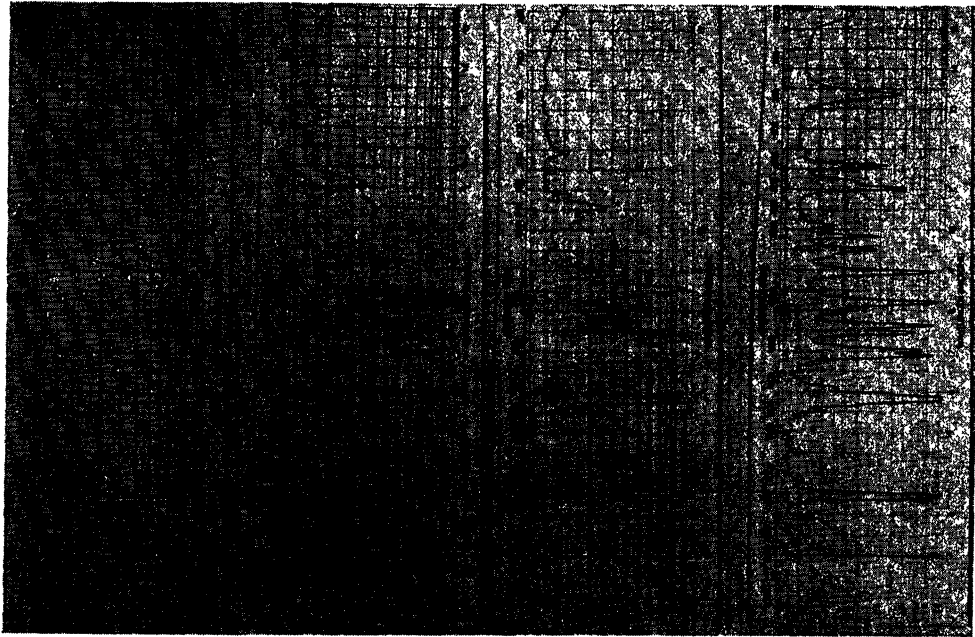
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Fig. 1d. Cont'd.

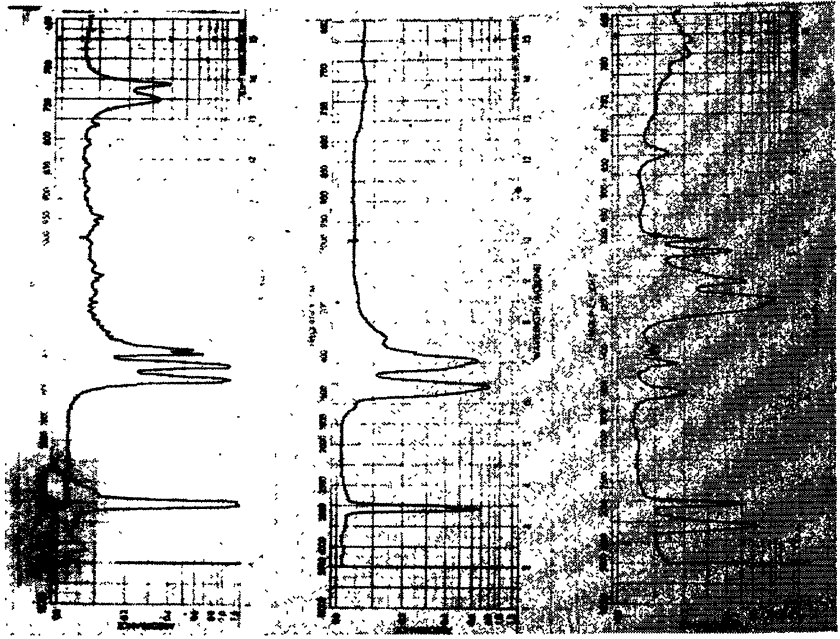


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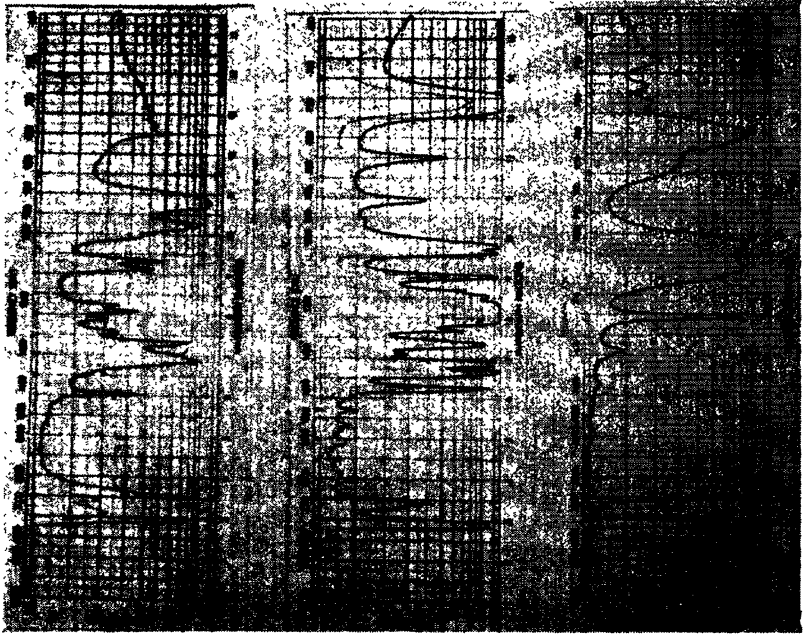


98.

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Fig. 1e



95.

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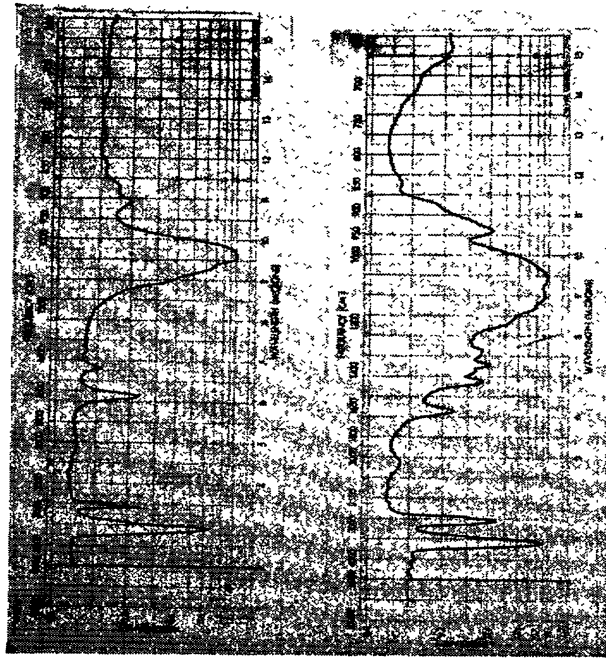
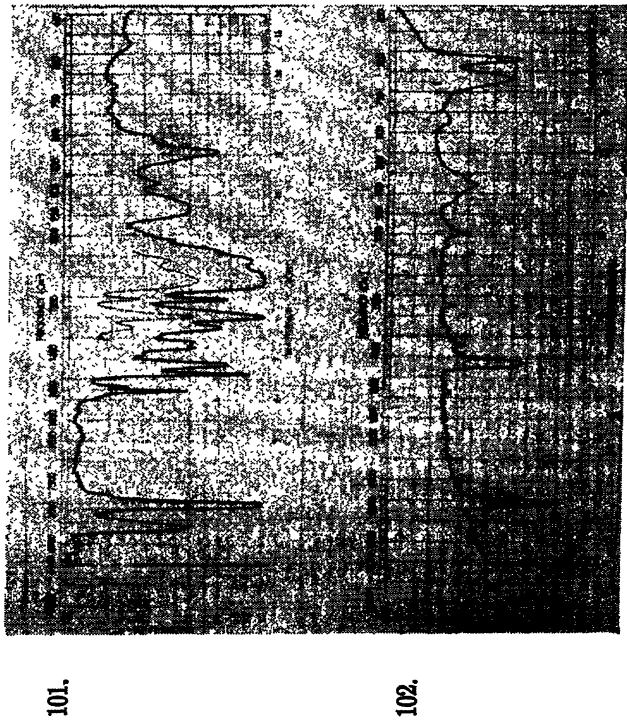


Fig. 1e. Cont'd.

INFRARED SPECTROPHOTOMETRY

whether they are inorganic or organic in nature. Spectra of each class are presented. The spectra of the following pigments exhibit no characteristic absorption bands and consequently are omitted:

White Pigments

Titanium-Calcium, $\text{TiO}_2 \cdot \text{CaSO}_4$ (spectrum is composite of both compounds)

Lithopone, $\text{ZnS} \cdot \text{BaSO}_4$ (spectrum characterizes only BaSO_4 portion)

Leaded zinc oxide, $\text{ZnO} \cdot 2\text{PbSO}_4 \cdot \text{PbO}$ (spectrum characterizes only PbSO_4 portion)

Zinc Oxide, ZnO (no absorption bands)

Yellow Pigments

Cadmium Lithopone, $\text{CdS} \cdot \text{BaSO}_4$ (only BaSO_4 portion exhibits bands)

TABLE 1. INFRARED ABSORPTION BANDS IN MICRONS FOR INORGANIC EXTENDERS AND WHITE, BLUE, YELLOW AND ORANGE PIGMENTS WITH SIMPLE SPECTRA

(s, strong; ms, medium strong; m, medium; w, weak)

1. Crystalline silica	8.55(w); 9.25(s); 12.55(m); 12.85(m); 14.45(m)
2. Diatomaceous earth (amorphous silica)	9.10(s, broad); 12.55(w)
3. Flaky talc	9.85(s); 15.00(ms)
4. Washed kaolin (KBr)	2.70(m, sharp); 9.05(s); [9.70, 9.90](s); 10.70(m); 10.95 (s); 12.65(w); 13.27(w); 14.30(m)
5. " " (mull)	2.73(m, sharp); [9.00, 9.67, 9.92](s); [10.67, 10.97] (ms); 12.65(w); 13.35 (w); 14.65(w, broad)
6. Mica	2.75(m); 9.75-10(s); 12.1(w); 13.35(w)
7. Pumice	9.00-10.00(s, very broad); 12.80(w)
8. Gypsum	[2.85, 2.95] (s); [5.95(w), 6.17(m)]; 8.5-9.15(s, broad); 15.00(m)
9. Marble	4.00(w); 5.55(w); 7.00(s, broad); 11.45(ms); 14.07(ms)
10. Barytes	[8.50, 8.95, 9.25] (s, broad); 10.18(w)
11. Blanc fixé (BaSO_4)	[8.42, 8.90, 9.30] (s sharp); 10.18(w)
12. Rutile, TiO_2	13-16(s, broad)
13. White lead	7.10(s); 14.70(ms)
14. Basic lead sulfate	[8.55, 9.25] (s, broad); 10.35(w)
15. Basic lead silicate	[9-10] (s, very broad); 12.55(m); 12.87(m); 14.45 (w)
16. Antimony trioxide	13.5(s, broad)
17. Iron blue	3.1(w) 4.8(s, sharp); 7.08(m)
18. Chrome yellow (KBr)	11.2-11.75(s, broad)
19. Chrome yellow (mull)	11.15-12.35(s, broad)
20. Chrome yellow (lemon)	9.0-9.55(s, broad); 11-12(s, broad)
21. Chrome orange (dark)	11.4-11.85(s, broad); 12.0(m)
22. Molybdate orange (dark)	9.30(m, broad); 11.65(s, broad)
23. Basic lead silico chromate	8.5-10(s, broad); 11.25-11.95(ms, broad); [12.6, 12.90] (ms); 14.45(m)
24. Zinc yellow	2.92(w); 3.1(w); 10.55(s); 11.1-11.4(s, broad); 12.30(s, broad); 14.05(s, broad)
25. Basic zinc chromate	2.90(s); 10.55-11(s, broad); 12.15(s, broad)
26. Strontium chromate	[10.80, 11.0, 11.25, 11.45, 11.85] (s)
27. Barium chromate	8.8(w); 9.0(w); 9.20(w); [10.7, 11.17, 11.47, 11.67] (s, broad)
28. Yellow hydrated iron oxide	[2.95, 3.20] (s); 11.05(s); 12.60(s)
29. Green chrome oxide	14.5-16(s, broad)
30. Bone black	4.96(w); [6.90, 7.1] (m); [9.20, 9.65] (s, broad); 10.40(w); 11.5(w)

TABLE 2. PAINT PIGMENT SAMPLES AND INFRARED SPECTRA

Yellow and Orange Pigments		
31	Hansa yellow, arylide of acetoacetic acid	(0.5 mg in KBr)
32	" " " " " "	(Mull)
Green Pigments		
33	Chrome oxide green, Cr_2O_3	(0.5 mg in KBr)
34	Phthalocyanine green, chlorinated copper phthalocyanine	(1 mg in ")
Red Pigments		
35	Para red, diazotized p-nitraniline coupled with beta naphthol	(0.5 mg in KBr)
36	" " " " " " " "	(Mull)
37	Toluidine red, diazotized m-nitro-p-toluidine coupled with beta naphthol	(0.5 mg in KBr)
38	Toluidine red, diazotized m-nitro-p-toluidine coupled with beta naphthol	(Mull)
39	Naphthol red, diazotized p-nitro-o-toluidine coupled with naphthol AS	(1 mg in KBr)
40	" " " " " " " "	(Mull)
41	Lithol red, Ba salt of diazotized tobias acid coupled with beta naphthol	(1 mg in KBr)
42	" " " " " " " "	(Mull)
43	B-O-N red, manganese salts of various amines coupled to 2-hydroxy-3-naphthoic acid	(1 mg in KBr)
44	B-O-N red, manganese salts of various amines coupled to 2-hydroxy-3-naphthoic acid	(Mull)
45	Alizarine red lake, alizarine dye precipitated on inert aluminum hydrate, calcium phosphate-sulfate base	(Mull)
Black Pigments		
46	Bone black, approx. 15% carbon with primarily calcium phosphate	(0.5 mg in KBr)

Blue Pigments

Ultramarine, $3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{Na}_2\text{S}$
(only the silicate portion is characterized)

Green Pigments

Chrome greens, mixture of chrome yellow and iron blue (spectrum is composite of both ingredients)

Red Pigments

Cadmium Red Lithopone, $\text{CdS} \cdot \text{CdSe} \cdot \text{BaSO}_4$ (only BaSO_4 exhibits absorption)

Red lead, Pb_3O_4 (no absorption bands)

Iron oxide, Fe_2O_3 (no absorption bands)

Black Pigments

Carbon black, elemental carbon (no absorption bands)

Iron black, Fe_3O_4 (no absorption bands)

Antimony black, Sb_2S_3 (only small absorption bands appear. These are believed to be due to impurities such as antimony carbonate and sulfate)

Mineral black, siliceous shale, 85 % fixed carbon (only the siliceous portion exhibits absorption bands)

Because of the relative simplicity of the spectra for inorganic extenders and some white, blue, yellow and orange pigments, only the absorption bands are listed in Table

INFRARED SPECTROPHOTOMETRY

1 for 30 samples. The pigments and spectra which are more complex are listed in Table 2. The actual spectra of Table 2 are reproduced in Fig. 1a.

Binders. The binders in a paint formulation are primarily resins and are classified

according to chemical structure and use. The spectrum of each resin was obtained with the material as a liquid, as a film cast from solution, or as a dispersion in KBr. All the films underwent a two hour treatment at 60°C in a vacuum oven. The water-based

TABLE 3. BINDERS AND INFRARED SPECTRA

Oils		
47	Linseed oil, raw	(liquid)
48	Oiticica oil	(liquid)
49	Tung oil	(liquid)
50	Castor oil, dehydrated	(liquid)
Alkyd Resins		
51	Linseed glycerol phthalate	(film)
52	Tallol ethylene glycol isophthalate	(film)
53	Styrenated soya tung glycerol phthalate	(film)
54	Vinyl tolunated soya tung glycerol phthalate	(film)
Amino Resins		
55	Melamine-formaldehyde, n-butylated	(film)
56	“ “ iso-butylated	(film)
57	Benzoguanamine “ n-butylated	(film)
58	Urea “ n-butylated	(film)
59	“ “ iso-butylated	(film)
Phenolic and Epoxy Resins		
60	<i>p</i> -tert-butylphenol-formaldehyde, alkali condensed	(1.4 mg in KBr)
61	<i>p</i> -phenylphenol-formaldehyde, acid condensed	(1.2 mg in KBr)
62	Epoxy modified Novolac (Epiphen 849 from Borden)	(1 mg in KBr)
63	Epoxy, bisphenol-epichlorohydrin type (epoxide equiv. approx. 200)	(1 mg in KBr)
64	“ “ “ “ “ 500)	(1 mg in KBr)
65	Epoxy ester (Dehydrated castor oil ester of Shell EPON 1004)	(film)
Lacquer Resins and Polymers		
66	Cellulose nitrate, RS type	(film)
67	Polyvinyl isobutyl ether	(film)
68	Polyvinyl chloride-acetate	(film, treated 125°C under vacuum)
69	Polymethyl methacrylate-butyl methacrylate	(film)
Emulsion		
70	Polyethyl acrylate-methyl methacrylate	(film on AgCl)
71	Polyvinyl acetate	(film “ “)
72	Polystyrene-butadiene	(film “ “)

resins were prepared on AgCl windows while the other films were prepared on NaCl windows.

The spectra of the binders are listed in Table 3.

Solvents. Solvents for paint products are usually classified according to chemical types. The solvent spectra listed in Table 4 were all determined in a sodium chloride sealed cell having a cell path of 0.028 mm.

Additives. Paint additives are materials

TABLE 4. SOLVENTS AND INFRARED SPECTRA

Aliphatic, Alicyclic, and Derivatives	
73	<i>n</i> -Heptane
74	Mineral spirits
75	Cyclohexane
76	Propylene tetramer
77	Perchloroethylene
78	1-Nitropropane
Aromatic Hydrocarbons	
79	Toluene
80	<i>o</i> -Xylene
81	<i>m</i> -Xylene
82	<i>p</i> -Xylene
Alcohols, Ether-Alcohols, Ketone-Alcohols	
83	<i>n</i> -Butanol
84	Isopropanol
85	Ethylene glycol mono-butyl ether
86	Diethylene glycol mono-butyl ether
87	Diacetone alcohol
Ketones	
88	Acetone
89	Methyl isobutyl ketone
90	Cyclohexanone
91	Isophorone
Esters and Ether-Alcohol Ester	
92	<i>n</i> -Butyl acetate
93	Amyl acetate
94	Ethylene glycol mono-ethyl ether mono-acetate

TABLE 5. ADDITIVES AND INFRARED SPECTRA

Anti-Skinning Agents		
95	Methyl ethyl ketoxime	(liquid)
96	Guaiacol	(liquid)
Agent for anti-flooding and general enhancement of good film formation		
97	Dimethyl silicone oil	(liquid)
Flatting Agent		
98	Zinc Stearate	(Mull)
Drier		
99	Manganese Naphthenate	(film on NaCl, dried 125°C Vacuum)
Surfactants		
100	Sodium alkyl aryl sulfonate, anionic	(1 mg in KBr)
101	Alkyl aryl ethylene oxide condensate, non-ionic	(liquid)
102	Alkyl dimethyl benzyl ammonium chloride, cationic (also a germicide and anti-static)	(film on AgCl, dried 105°C)
Thickening Agents		
103	Specially modified clay (for organic systems)	(0.3 mg in KBr)
104	Methyl cellulose (for aqueous systems)	(2 mg in KBr)

which are added to paint products in small quantities to bring about some otherwise unattainable property. The spectra of typical additives are listed in Table 5.

JAMES D. MCGINNESS AND
CLAUDE A. LUCCHESI

PHASE TRANSITION MEASUREMENTS*
OF WAXES

A method based on infrared absorption in the 13- to 14-micron region has been developed for determining transition temperatures of commercial waxes. The melting temperature and the temperatures at which solid phase transitions occur can be obtained in 30 to 45 minutes on as little as 1 gram of sample.

Certain properties of commercial waxes, such as tensile strength, ductility, seal strength, and blocking characteristics, change markedly with changes in crystal structure. It is important, therefore, to develop rapid and convenient methods for detecting both these crystalline changes and the temperatures at which they occur. Such methods can be applied in studying the relationship between the performance properties and compositional or structural changes occurring in commercial paraffin waxes.

The phase transitions of normal paraffins have been determined in a variety of ways.^{1, 6-9} Templin,¹³ who measured the thermal expansion of paraffins and petroleum waxes, found significant volume changes for paraffin waxes at the melting point and at about 10°C below the melting point. He also refers to a number of important investigations. A refractometric method for determination of phase transformations in commercial paraffin waxes is reported by Johnson.⁴

Infrared studies of polyethylenes, glycerides, etc., revealed that abrupt changes in the infrared spectra sometimes occur as the result of polymorphic crystalline phase transitions.^{2, 3, 5, 11} The changes in absorption characteristics were particularly marked in the 13.5- to 14.0-micron region. The authors observed such changes in a large number of commercial paraffin waxes. The change occurs as a splitting of the 13.88-micron

methylene rocking vibration^{10, 12} into a 13.72- and 13.92-micron doublet at the transition temperature. This phenomenon has been utilized in developing a rapid method for measuring the transition temperatures of commercial waxes.

Apparatus

The infrared measurements were obtained with a single-beam, Beckman IR-2 spectrophotometer equipped with sodium chloride optics. The sample cell is similar in size and basic design to a cell manufactured by the Beckman Instrument Co. "Nichrome" heating elements were wound in each of the "Transite" cell-assembly plates for reheating or slowing down the cooling rate of the sample. Temperature measurements were made with an iron-constantan thermocouple recessed in a V-shaped groove just below the inner surface of one of the salt windows. This arrangement permitted intimate contact between sample and thermocouple, thus minimizing temperature lag. Cooling of the sample to the transition temperature was controlled by introducing dry nitrogen through a piece of perforated copper tubing attached to one side of the cell holder. The dry nitrogen vapor was blown through the perforations and onto the cell. If the transition temperature was below ambient, the nitrogen was precooled by passage through a coil placed in a temperature control bath. The sample cell was loaded by introducing a liquid sample into the preheated cell from a heated hypodermic syringe.

Exploratory

A sample of 138-40°F (ASTM) melting point, fully refined commercial paraffin (FRP) wax was chosen for the initial study of phase transition. Infrared spectra of the wax exemplify the effect of temperature on the infrared absorption at the 13.73-micron position. The spectrum of the wax, scanned in the solid phase but above the transition temperature, shows a single absorption band

* Abridged from paper in *Analytical Chemistry*, **30**, 1005 (1958); by permission.

at 13.88 microns. The spectrum from a scan obtained below the transition range clearly exhibits the doublet at 13.73 and 13.92 microns.

The infrared measurements of transition range were checked by a differential thermal analysis that established the occurrence of a phase change at the temperature of the infrared band splitting. X-ray measurements made above and below the transition temperature also confirmed this phase change.

Method

Transition temperatures were determined at the fixed wave length of 13.73 microns. The instrument slit width was adjusted to give an initial transmittance level of at least 50% T with the molten wax sample. Recording of the transmittance was begun immediately as the molten sample was placed in the light path. The cooling was adjusted between the melting point and transition point to provide a rate of fall of 2° to 3°F per minute. The transmittance was recorded continuously until after the phase transition had been completed. Temperature of the sample was recorded at intervals of approximately 1°F.

The melting point may be obtained from the cooling curve as the temperature at the initial deflection from the transmittance plateau established above the solidification point. The temperature of this point is interpolated to the nearest 0.5°F. The transition temperature is picked in a similar manner, using the plateau established between the melting and transition points.

Analytical Results

Table 1 gives the transition measurements for several commercial waxes. The reproducibility of the infrared method was $\pm 0.5^\circ\text{F}$. Transition temperatures by other methods were not available; however, the temperatures determined on several n -paraffins by the infrared method when compared with the data of Templin,¹³ obtained by

TABLE 1. MELTING AND TRANSITION TEMPERATURE DATA FOR REFINERY WAXES

Wax Sample	Melting Temp., °F.			Transition Temp., °F., Infrared Method
	Infrared method	ASTM method 87-42	Δ	
138/140°F. FRP wax A	139.5	138.8	0.7	114.5
123°F. FRP wax	124.0	123.2	0.8	102.0
118°F. FRP wax	120.5	118.8	1.7	101.0
138/140°F. FRP wax B	139.0	139.1	0.1	112.0
124/126°F. FRP wax	125.0	125.2	0.2	88.5
Heavy wax	156.5	156.8	0.3	138.0
HMP ^a wax	182.5	184.8	2.3	...

^a High melting point wax.

volume expansion measurements, show reasonable agreement. The infrared method will also determine melting points with a reproducibility of $\pm 0.5^\circ\text{F}$ which correlate well with measurements by ASTM Method 87-42.

Parallel with these studies of commercial waxes was an analysis of infrared absorption of pure crystalline n -paraffin hydrocarbons (*Spectrochimica Acta*, 12, 12 (1958).

A number of pure n -paraffins (C_{17} – C_{36}) have been studied in the 650–800 cm^{-1} infrared region. Differences were obtained between paraffins of odd and even carbon numbers at temperatures below that of the solid phase transitions. Spectra of the odd carbon number n -paraffins below C_{26} , and both odd and even carbon number n -paraffins above C_{26} are characterized by a splitting of the 721 cm^{-1} band into a 718–728 cm^{-1} doublet. The even carbon number n -paraffins below C_{26} are characterized by a single absorption band at 715 cm^{-1} . The observations are related to other published information concerning crystal structures and infrared absorptions of paraffins and long hydrocarbon chain polymers.

C_{22} and C_{24} normal paraffins were blended to obtain mixtures for testing the effects of

mixing. Use of these two even carbon number normal paraffins is of special interest since each shows the single 715 cm^{-1} absorption band below the transition temperature. The addition of only 4 per cent wt. of C_{22} results in the occurrence of the high-frequency component though it is of much lower intensity than the low-frequency band. The increase in intensity of the high-frequency component with increasing concentration of C_{22} is also observed. The two bands reached equal intensity at 15 per cent wt. of C_{22} with a further increase to 50 per cent wt. producing no additional change.

Of considerable interest also is the fact that the position of the low-frequency component migrates from 715 cm^{-1} as the concentration of C_{22} is increased. The degree of band splitting is observed to be dependent upon both concentration and chain length of the minor component. Similar observations of the effect of concentration on degree of band splitting have also been reported in earlier work.

The effect of chain length was further emphasized by blending <5 per cent of C_{27} in C_{24} . The fully formed doublet was observed with both components exhibiting equal intensity at 718 and 728 cm^{-1} . These results obtained from increasing chain length may indicate a folding of the longer chain ends into the interstices of the crystal lattice in such a way as to prevent close packing of the unit cell. A similar explanation is given for results obtained from X-ray studies.

REFERENCES

1. ANDREW, E. R., *J. Chem. Phys.*, **18**, 607 (1950).
2. CHAPMAN, D., *Nature*, **176**, 216 (1955).
3. ELLIOTT, A., AMBROSE, E. J., AND TEMPLE, R. B., *J. Chem. Phys.*, **16**, 877 (1948).
4. JOHNSON, J. F., *Ind. Eng. Chem.*, **46**, 1046 (1954).
5. KENDALL, D. N., *Anal. Chem.*, **25**, 382 (1953).
6. KOOLVOORT, J., *J. Inst. Petrol.*, **24**, 338 (1938).
7. MAZEE, W. M., *Rec. trav. chim.*, **67**, 197 (1948).
8. PIPER, S. H., CHIBNALL, A. C., HOPKINS, S. J., POLLARD, A., SMITH, J. A. B., AND WILLIAMS, E. F., *Biochem. J.*, **25**, 2072 (1931).

9. SEYER, W. F., PATTERSON, R. F., AND KEAYS, J. L., *J. Am. Chem. Soc.*, **66**, 179 (1944).
10. SHEPPARD, M. AND SUTHERLAND, G. B. B. M., *Nature*, **159**, 739 (1947).
11. STEIN, R. S. AND SUTHERLAND, G. B. B. M., *J. Chem. Phys.*, **22**, 993 (1954).
12. SUTHERLAND, G. B. B. M. AND JONES, A. V., *Nature*, **160**, 567 (1947).
13. TEMPLIN, P. R., *Ind. Eng. Chem.*, **48**, 155 (1956).

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POLARIZED INFRARED SPECTROSCOPY

The usefulness of infrared spectroscopy for the investigation of varied chemical and physicochemical problems is well recognized. A more specialized adaption which is of advantage in many problems is the utilization of plane polarized infrared radiation. The absorption of this radiation by a solid species reveals information about the direction of transition moments of atoms and groups of atoms in a molecule and can therefore be related to the modes of vibration which give rise to various absorptions in the infrared region of the spectrum. The absorption band associated with a vibrational mode of a molecule is most intense when the plane of vibration of the radiation is parallel to the direction of the transition moment. Since these moments are usually related to some bond direction or motion of a group, measurements with polarized infrared radiation have helped to give an improved three-dimensional view of molecules. For example, polarized infrared studies have shown that bulky substituents *ortho* to a nitro group on a benzene ring cause the nitro group to rotate out of its normal position of planarity with the benzene ring. Other things such as the complete coplanarity of the urea molecule and the differentiation between folded and extended forms of protein molecules have also been shown with polarized infrared

radiation. These and other examples are discussed in more detail below.

One of the first workers to experiment with polarized infrared light was Pfund¹ and in 1906 he introduced the first selenium reflection polarizer. There was a period of relative inactivity and forty-one years later Pfund described an improved selenium reflection polarizer.² In recent years the number of publications describing infrared radiation polarizers and research with polarized infrared radiation has increased many-fold corresponding to the greater use of infrared spectrometers and the availability of inexpensive polarizer attachments for these instruments.

The most useful method of producing plane polarized light in the visible, ultraviolet and near infrared (up to 2.6 microns) region of the spectrum has been by double refraction, by utilizing anisotropic materials such as calcite (Nicol prism) and quartz. These materials, however, absorb normal infrared radiation so that in order to construct a Nicol type prism that would be suitable in the useful infrared region, we must have a crystalline material which is birefringent and transparent in this region. None of the usual infrared optical materials

have these qualities, therefore, this method is not useful for producing plane polarized infrared radiation. Polarization by reflection and refraction is more applicable in this region.

In 1808 Malus showed that if white light was incident upon the polished surface of a plate glass, the reflected beam was partially plane polarized. At a specific angle, the polarizing angle, the reflected beam was 100 per cent plane polarized. Figure 1a shows the case where unpolarized light is incident to a glass surface. The angle of incidence is not the polarizing angle. The reflected component is richer in one vector component (parallel to the surface of incidence and perpendicular to the plane of the page) and the refracted ray is richer in the other component perpendicular to the surface of incidence. In Figure 1b the light is incident at the polarizing angle in which case all of the reflected component is pure, i.e., the parallel vector, however, not all of the parallel vector has been reflected. Therefore, the refracted ray contains the perpendicular component in addition to the parallel component which was not reflected. Brewster discovered that at the polarizing angle the reflected and refracted rays were 90° apart. Thus the polariz-

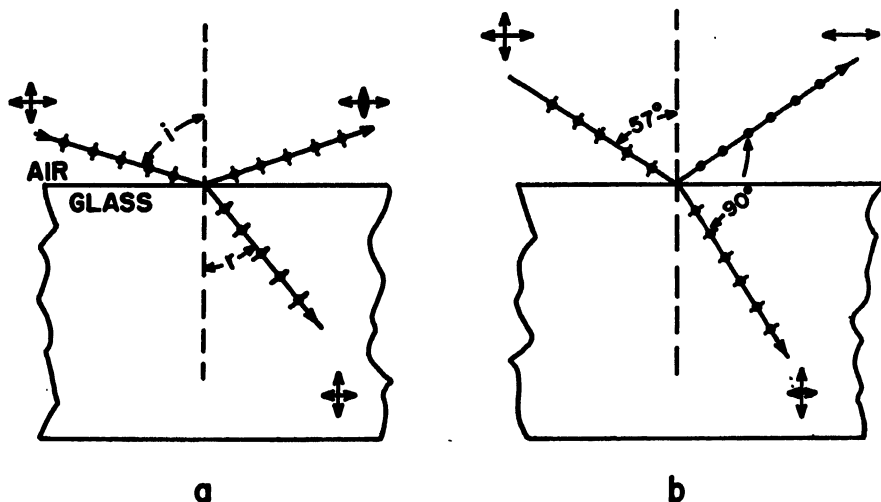


FIG. 1. Polarization of light by reflection at a glass surface.

INFRARED SPECTROPHOTOMETRY

ing angle can be correlated with the index of refraction of any material. At the polarizing angle, $i + r = 90^\circ$ and $\sin r = \cos i$. From Snell's Law, $n = \sin i / \sin r$ or $n = \sin i / \cos i = \tan i$. The angle of polarization is, therefore, dependent on the refractive index of the material. Also the intensity of reflected light increases proportionally with an increase in the refractive index of different materials.³ Actually, reflection at Brewster's angle (the polarizing angle) is an effective method of securing plane polarized infrared radiation over a useful range.

Figure 2 shows a selenium type reflection polarizer similar to the type used by Pfund.² Disadvantages of this type polarizer are that it transmits only 27 per cent of the original unpolarized beam intensity and that placement of this type of polarizer with respect to

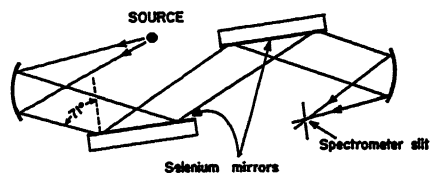


FIG. 2. Selenium-type reflection polarizer for infrared radiation.

the spectrometer and sample is usually inconvenient.

Transmission polarizers are more commonly employed now for the infrared region. This type polarizer consists of a series of silver chloride or selenium plates arranged so that instead of the reflected component being utilized, the refracted component is used. Figure 3 shows the behavior of the light as it passes through a transmission polarizer. The incident unpolarized radiation may be treated as though the waves are vibrating in two mutually perpendicular planes. Those waves vibrating parallel to the plane of the page, incident at the polarizing angle, are all refracted. The waves vibrating perpendicular to the plane of this page are partially reflected and the remainder refracted. Thus the refracted ray contains some radiation in both planes of polarization. With a pile of such plates, the net result is that the refracted beam on passing through the pile loses more and more of the component which is perpendicular to the page and becomes purer in the other component. The fractional polarization of the radiation transmitted through a pile of m plane parallel plates of dielectric, with refractive index n ,

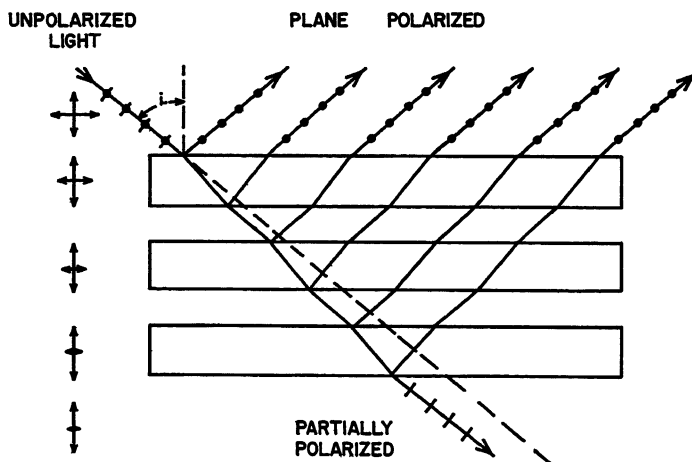


FIG. 3. Behavior of radiation on passing through a series of parallel plates oriented to the radiation at the polarizing angle (i).

which are oriented at Brewster's angle is given by the expression⁴

$$p = \frac{m}{m + \left(\frac{2n}{1 - n^2}\right)^2}$$

This expression takes account of the multiple reflections which occur at the different surfaces ($2m$ surfaces). From the equation it can be seen that the degree of polarization increases with the number of plates and with an increase in refractive index. However, m is practically limited due to loss of intensity by absorption in the plates. Most of the polarizers utilize about 6 plates, but there have been reports in the literature in which 10 plate polarizers were employed. As mentioned before, silver chloride and selenium are useful plate materials. The degree of polarization is better than 98 per cent with a six pile polarizer, with transmissions up to 47 per cent of the original unpolarized radiation.

Selenium polarizers are more fragile since the plate thickness must be in the order of 4 microns in order to cut down on absorption losses. The fabrication of this type polarizer has been described.⁵ The thin selenium films are vacuum deposited on cellulose nitrate film. This base film is removed by dissolving in acetone.

A silver chloride pile transmission polarizer (Figure 4) has been described by Newman and Halford⁶ who used 6 plates of 0.020 inch thickness. An appreciable displacement of the beam arises from the refraction at each surface of the plates. The displacement is negligible in the selenium transmission polarizer since these films are very thin. A rearrangement of the silver chloride plates has been described, so that there is no displacement of the beam^{7, 8} (Figure 5). The silver chloride does not darken appreciably due to actinic action from normal Nernst or globar sources, but must, of course, be shielded from room light. Transmission polarizers are commercially

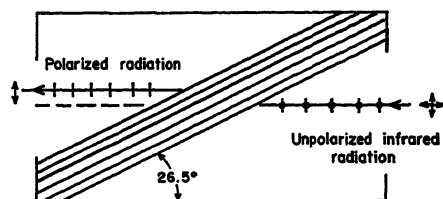


FIG. 4. A typical arrangement of silver chloride films in a polarizer.

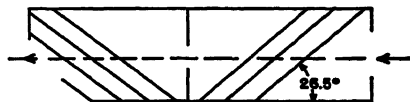


FIG. 5. Arrangement of silver chloride films according to Makas and Shurcliff (ref. 7).

available from most of the manufacturers of the various infrared spectrometers.

In the near infrared region polarization can be secured by selective absorption (dichroic polarizers). Calcite is useful as an absorption polarizer at about 4 microns. A plastic polarizing film is available which is useful from 0.8 to 2.2 microns.⁹

In the far infrared region wire or echelette gratings secure partially polarized light.^{8, 10, 11}

Sample Preparation. Crystalline materials may not need any further preparation if the crystal section is thin enough and of sufficient area. Crystals which are too thick can be cut and polished. If possible, the cuts should be made in the direction that is parallel or in known orientation to one of the principal axes. Ideally, it is desirable to examine any crystal in the form of several thin sections, each containing the various pairs of crystal axes. A technique for obtaining thin oriented crystalline specimens in large enough area for normal macro measurements, is that of allowing molten material to crystallize subject to a temperature gradient. Halverson and Francel¹² have used this technique. Two potassium bromide windows with a 0.01-mm spacer are filled with the warm melted sample. One edge of the assembly rests on a small heater and the opposite edge rests on a water cooled metal

bar. The heater is allowed to cool, and since it cools rather slowly, a temperature gradient is set up along the cell. As the cool end approaches the freezing point, it is seeded with a small crystal. All the crystals which form tend to be oriented in the same direction, so that in all respects, the final form is analogous to a thin single oriented crystal.

Zwerdling and Halford¹³ have reported a useful method for growing single crystals from the vapor phase. They were able to produce and study crystalline benzene at low temperatures, utilizing polarized infrared radiation.

Flat thin crystals of anthracene, naphthalene and biphenyl have been formed from solution, by a technique which creates a temperature and pressure gradient in the solution.¹⁴ Various techniques of forming large crystals are discussed in specialized texts,¹⁵ and such crystals when cut and ground to the required size make excellent specimens.

The preparation of thin and oriented polymer films of sufficient area may be accomplished by several methods. The most common method is by stretching a film of suitable thickness. The degree of stretching to produce orientation may vary from 50 per cent to 500 per cent or more. Many of the polymers on stretching do not change much in thickness, but instead tend to "neck," i.e., the width of the film becomes narrower. The per cent of stretching can be simply determined by marking off divisions on the unstretched film and measuring the separation after stretching. In some cases, the stretching and orientation are improved when carried out at higher temperatures. Another useful technique is rolling. The rolling may be carried out directly upon the polymer film, or the film may be placed or melted between two thin sheets of silver chloride, and then rolled. Silver chloride is soft enough so that it stretches with the polymer. The infrared measurements can be made with the silver chloride in place, or if

desirable, the silver chloride can be removed easily by dissolving in sodium thiosulfate.

Either stretching or rolling causes the polymer chains to be oriented in the stretching or rolling direction. The enhancement of orientation in the crystalline regions can be determined by x-ray examination.

Sample Measurement. As in nonpolarized infrared measurements, the sample is placed where the beam diameter is the smallest, just before the entrance slit, and placed so that it is oriented to the slit direction in a specific way, e.g., direction of crystal growth or direction of stretch parallel to the slit. Most of the polarizers are designed so that they are usually placed in the optical path so as to polarize the radiation before it passes through the sample. One exception is the polarizer described by Makas and Shurcliff⁷ which is placed in a more efficient position between the sample and monochromator. In order to measure the sample with the two mutually perpendicular electric vectors, either the sample is rotated through 90°, or the polarizer is rotated through the same angle. Quite often the sample is not uniform, for example in thickness, so that when the sample is rotated, it does not present the same section. For exact work with such samples, the polarizer is rotated. A disadvantage which occurs when the polarizer is rotated, is that there are different energy transmission values for different electric vectors through the spectrometer. This occurs because of the many reflecting components in the spectrometer itself, which leads to some depolarization and preference for certain vector components. One technique which usually gives equal energy transmission as the polarizer is rotated through 90° is to adjust the polarizer so that the vibration plane of the electric vector is 45° to the spectrometer slit for one measurement. The polarizer is then rotated through 90° to a position 45° on the other side of the slit for the second measurement. Under these conditions the radiation may

become elliptically polarized to a slight degree.

Another useful method for examining polymer films is to mount the sample so that it can be tilted about the vertical axis, parallel to the slit. An example will be described further on.

In many cases the sample size is limited to a fiber or a minute crystal. On these occasions a micro illuminator designed for infrared measurements can be used to advantage with polarized radiation. One difference between macro and micro measurements which should be pointed out is that in the macro measurements the radiation which passes through the sample is essentially parallel, whereas in micro measurements the sample is at the focal point and the radiation passing through the sample is convergent. For example, in Figure 6, there arises a situation where the transition moment of an N—H group lies perpendicular to the surface of radiation incidence (plane def). No absorption of this moment occurs with the electric vector "a" (in plane lmn) which is parallel to this moment. However, when the radiation is convergent, then the resultant electric vector "b" (also in plane

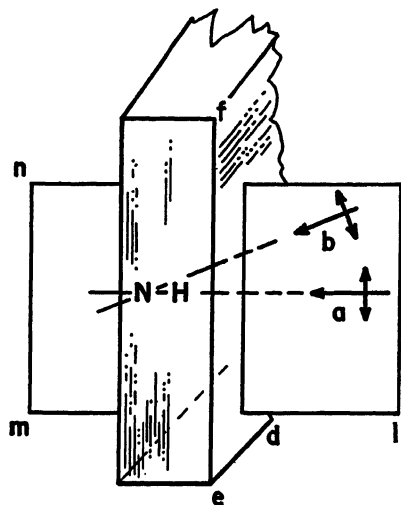


FIG. 6. Effect of convergence. The N—H group lies within crystal in the plane lmn.

lmn) does give rise to an absorption band. The subject of convergence has been treated by Wood¹⁶ and Fraser.¹⁷ If awareness of the effects of convergence is appreciated, then the spectra so obtained are very useful.

Either single beam or double beam spectrometers are utilized for polarized infrared measurements. When making measurements on a single beam instrument, or a double beam instrument being used as a single beam instrument, the reference curves are obtained with the polarizer in the light path adjusted so that the plane of vibration is in the desired direction. The sample is removed from the radiation path. As in ordinary measurements, the light path should be masked similarly as the sample. In double beam measurements a second polarizer is inserted in the reference beam, or the reference beam is compensated by appropriate masking. Double beam microscope systems have been briefly reviewed by Wilkinson *et al.*¹⁸

Dichroism is observed when the transition moment of a group lies in a direction so that different orientations of the plane polarized light are absorbed in varying degrees. The dichroic ratio of an absorption band is experimentally determined by measuring the ratio of absorptivity for plane polarized radiation in one direction to the absorptivity of plane polarized radiation 90° away from the original direction. The type of dichroism, i.e., parallel or perpendicular, is a relative term, and must be related to the orientation of the sample, e.g., relation of a crystalline axis with spectrometer slit or stretching direction of a film. A quantitative value for the dichroic ratio is obtained only when the sample is crystalline, perfectly oriented, and properly aligned with respect to the incident radiation. Errors in measurements have been discussed in detail by Charney.¹⁹

Examples of Applications of Polarized Infrared Radiation. Some examples from the literature are discussed so that researchers may better appreciate the potential

uses of polarized infrared spectroscopy and familiarize themselves with techniques. A bibliography of recent studies on various materials has been given by Gore²⁰ and there has been a brief review of this subject.¹⁸ The subject of dichroism and crystal structure, including theory and applications, has been summarized by Mathieu.²¹

Most of the earlier work utilizing polarized infrared radiation dealt with inorganic materials. The purpose was usually to establish fundamental frequencies, to study bond angles, and for completing and confirming crystal structure data, obtained from x-ray studies.

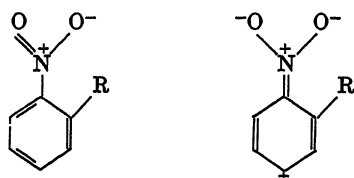
Quantitative polarization studies were made of potassium gold dicyanide in order to determine the inclination of the linear N—C—Au—C—N group with the crystalline C axis.²² The crystals were mounted with the C axis perpendicular to the direction of the propagation of light and parallel to the slit direction. The combination band at 2586 cm⁻¹ (summation of the asymmetric C—N stretching vibration at 2140 cm⁻¹ and the symmetric Au—C stretching vibration at ca 446 cm⁻¹) was studied. This band which is polarized in the same direction as the fundamental at 2140 cm⁻¹, allowed the use of thicker crystals. After establishing that Beers' law held for the slit widths and crystal thickness employed, the optical densities with polarized radiation were determined with the light parallel and perpendicular to the C axis. From the equation

$$\frac{OD\ 90^\circ}{OD\ 0^\circ} = \frac{1}{2} \tan^2 \alpha$$

the angle of inclination, α , was found to be 28°. Similarly the value for potassium silver dicyanide was found to be 27°.²³

An interesting application is given in the work of Francel who determined the geometry of the nitro group, on a benzene ring, in the presence of *ortho* substituents.²⁴ In the absence of steric effects the nitro group is coplanar with the phenyl ring because of

resonance between the ring and the nitro group as follows:



However, a large enough *ortho* group could rotate the nitro group plane out of the plane of the phenyl ring. A series of *ortho* substituted nitrobenzenes was studied.

The nitro group gives rise to a symmetrical and an asymmetrical stretching vibration, at 1360 and 1540 cm⁻¹, respectively, which have transition moments as shown in Figure 7. Fortunately the nitrobenzenes crystallize so that the planes of the phenyl rings are perpendicular to the direction of crystal growth. Figure 8 shows an isolated molecule and its orientation for measurement. When the nitro group is coplanar, both the symmetrical and asymmetrical stretching vibrations should show perpendicular dichroism, i.e., the absorptions of both the 1360 and 1540 cm⁻¹ bands will be more intense when measured with the perpendicular vector (Figure 8) than with the parallel vector. As the nitro group rotates out of the plane of the phenyl ring, the symmetrical stretching vibration should still exhibit perpendicular dichroism, but the asymmetrical stretching vibration should show parallel dichroism.

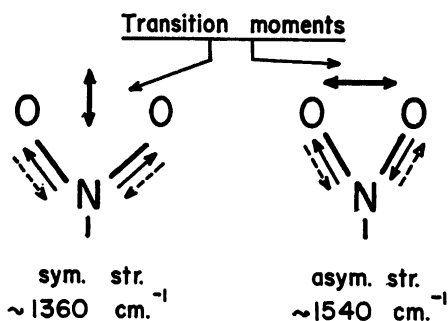


Fig. 7. Direction of transition moments for symmetrical and asymmetrical stretching vibrations of the nitro group.

Table 1 summarizes the results which showed that the chloro and bromo groups *ortho* to the nitro group were large enough so that steric hindrance prevented coplanarity of the nitro group and the phenyl ring.

Waldron and Badger²⁵ showed that the urea molecule is completely coplanar by resolving four fundamental N—H valence frequencies in the $3\ \mu$ region as shown in Figure 9. For the non-planar molecule only three of these fundamentals should be active. In unpolarized radiation two absorption bands at 3436 and 3333 cm^{-1} appear and it is only when the radiation is polarized that these two bands are resolved into their components.

In many cases it has been possible to assign the type of vibration to some of the fundamental frequencies. For example proteins, polypeptides and nylon all show a band at 700 cm^{-1} which was assigned to either an in-plane or out-of-plane NH deformation. The dichroism of this band was studied by Kessler and Sutherland²⁶ utilizing oriented nylon films. It was found that the intensity of the absorption was greatest with the electric vector perpendicular to the stretching direction. From x-ray studies it was known that the nylon crystalloids con-

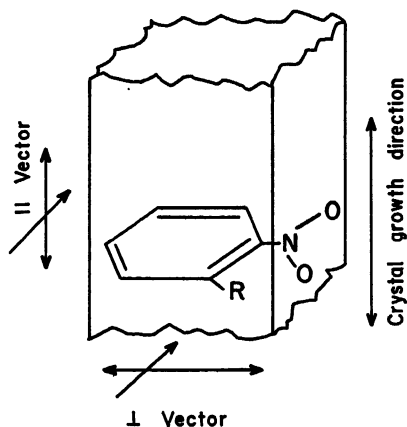


FIG. 8. Section of a nitrobenzene group showing its orientation in crystal and directions of incident electric vectors.

TABLE 1. POLARIZATIONS OF NITRO GROUP STRETCHING VIBRATIONS IN SUBSTITUTED NITROBENZENES²⁴

Compound	NO ₂ stretching vibration	Polarization
<i>o</i> -Nitrophenol	symmetrical	perpendicular
	asymmetrical	perpendicular
2-Nitroresorcinol	symmetrical	perpendicular
	asymmetrical	perpendicular
<i>o</i> -Nitroaniline	symmetrical	perpendicular
	asymmetrical	perpendicular
<i>o</i> -Nitrobromobenzene	symmetrical	perpendicular
	asymmetrical	parallel
<i>o</i> -Nitrochlorobenzene	symmetrical	perpendicular
	asymmetrical	parallel

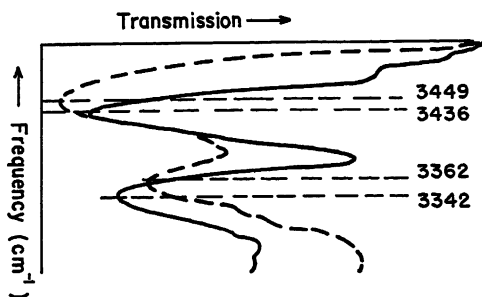


FIG. 9. Polarized spectra of urea crystal. Solid curve, electric vector perpendicular to tetragonal axis; dashed curve, electric vector parallel to tetragonal axis (ref. 25).

sisted of parallel sheets, with backbone planes lying in the sheets and adjacent chains held together by internal hydrogen bonds. These extend perpendicular to the chain axis. An in-plane deformation would exhibit parallel dichroism (Figure 10). Observation of perpendicular dichroism indicated that this vibration was due to an out-of-plane deformation.

Most of the more recent investigations have been directed to polymeric materials. Studies with oriented films have led to information about the orientation of specific groups to the polymer chain, configuration of the chain axis and crystallinity.

The folded and extended forms of proteins and polypeptides can be differentiated with polarized radiation. The NH stretching

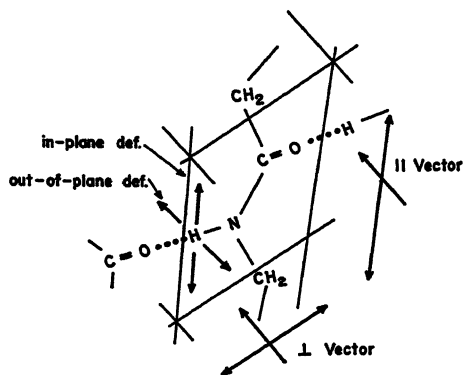


Fig. 10. Oriented nylon film. The stretching direction and the spectrometer slit are in the same direction as the parallel ($\parallel$) vector.

vibrations at 3310 and 3060 cm^{-1} show parallel dichroism for α and β keratins, polyglutamic esters, myosin and tropomyosin which are believed to be in the folded form, whereas in the extended form which feather keratin assumes, these absorptions show perpendicular dichroism.²⁷ Similarly the NH deformation and C=O stretching modes show orientation changes in the different forms. The techniques have been reviewed recently.²⁸

The technique utilizing tilted oriented films has been applied to the determination of benzene ring orientation in polyethylene terephthalate films.²⁹ Radiation with the plane of vibration perpendicular to the spectrometer slit was used in the following measurements. The polymer was stretched and mounted so that the stretching direction was parallel to the electric vector and the film was rotated about the vertical axis, parallel to the slit. As the sample was tilted it was observed that bands at 730 and 875 cm^{-1} , corresponding to CH out-of-plane bending modes, increased in intensity. When the sample film was mounted so that the stretching direction was perpendicular to the electric vector and the sample again tilted, as before, the same bands showed relatively smaller increases in intensity. These observations indicate that the ben-

zene ring planes are oriented in the direction of stretching, but randomly with respect to the film surface. When a specimen was stretched along one direction and then perpendicular to this direction, the 730 and 875 cm^{-1} bands increased on tilting, but the intensity of the CH in-plane bending mode at 1020 cm^{-1} decreased. The behavior indicates that in the doubly oriented film, the benzene rings are oriented with their planes essentially parallel to the film surface.

The infrared flow dichroism of polymers in solution was studied by a recently developed technique.³⁰ Many of the natural polymers exist primarily in solution so that this method is important. The polymer solution was pumped through a modified infrared liquid cell which was placed so that the flow direction was parallel to the spectrometer slit. Sufficient hydrodynamic orientation was obtained with poly- γ -benzyl-L-glutamate so that the N—H stretching vibration at 3300 cm^{-1} showed strong parallel dichroism. The principal use of this method will be for inferring detailed molecular configurations in solution.

REFERENCES

1. PFUND, A. H., Johns Hopkins Univ. Circular No. 4, **13** (1906) or *Ap. Jn'l.* **24**, 19 (1906).
2. PFUND, A. H., *J. Optical Soc. Am.*, **37**, 558 (1947).
3. A more comprehensive discussion of the polarization of light may be found in a text on optics, for example, "Fundamentals of Physical Optics," F. A. Jenkins and H. E. White, McGraw-Hill Co., New York, 1950.
4. PROVOSTAGE and DESAINS, *Ann. Chim. Phys.*, **30**, 159 (1850).
5. ELLIOTT, A., AMBROSE, E. J., and TEMPLE, R., *J. Opt. Soc. Am.*, **38**, 212 (1948).
6. NEWMAN, R. and HALFORD, R. S., *Rev. Sci. Instrum.*, **19**, 270 (1948).
7. MAKAS, A. S. and SHURCLIFF, W. A., *J. Optical Soc. Am.*, **45**, 998 (1955).
8. YAMAGUCHI, A., ICHISHIMA, I., and MIZUSHIMA, S., *Spectrochim. Acta*, **12**, 294 (1958).
9. Infrared Linear Polarizer, Type HR, Polaroid Corp., Cambridge 39, Mass.
10. MEECHAM, W. C., *J. Appl. Phys.*, **27**, 361 (1956).

11. MEECHAM, W. C. AND PETERS, C. W., *J. Appl. Phys.*, **28**, 216 (1957).
12. HALVERSON, F. AND FRANCEL, R. J., *J. Chem. Phys.*, **17**, 694 (1949).
13. ZWERDLING, S. HALFORD, R. S., *J. Chem. Phys.*, **23**, 2221 (1955).
14. HALLMAN, H. AND POPE, M., "Technical Report on Preparation of Thin Anthracene Single Crystals," ONR Contract No. 285 (25) June 9, 1958.
15. For example see H. E. Buckley, "Crystal Growth," John Wiley and Sons, Inc., 1951.
16. WOOD, D. L., *Ann. N. Y. Acad. Sci.*, **69**, Article 1, 194 (1957).
17. FRASER, R. D. B., *J. Chem. Phys.*, **21**, 1511 (1953).
18. WILKINSON, G. R., PRICE, W. C., AND BRADBURY, E. M., Proceedings of the Conference on Molecular Spectroscopy, *Spectrochim. Acta*, **14**, 318 (1959).
19. CHARNEY, E., *J. Optical Soc. Am.*, **45**, 980 (1955).
20. GORE, R. C., *Anal. Chem.*, **30**, 570 (1958).
21. MATHIEU, JEAN-PAUL, *J. Phys. Radium*, **16**, 219 (1955).
22. JONES, L. H., *J. Chem. Phys.*, **22**, 1135 (1954).
23. JONES, L. H., *J. Chem. Phys.*, **25**, 379 (1956).
24. FRANCEL, R. J., *J. Am. Chem. Soc.*, **74**, 1265 (1952).
25. WALDRON, R. D. AND BADGER, R. M., *J. Chem. Phys.*, **18**, 566 (1950).
26. KESSLER, H. K. AND SUTHERLAND, G. B. B. M., *J. Chem. Phys.*, **21**, 570 (1953).
27. AMBROSE, E. J., ELLIOTT, A., AND TEMPLE, R. B., *Nature*, **163**, 859 (1949).
28. ELLIOTT, A., *J. Appl. Chem.*, **8**, 341 (1956).
29. LIANG, C. Y., AND KRIMM, S., *J. Chem. Phys.*, **27**, 327 (1957).
30. BIRD, G. R., PARRISH, M., JR., AND BLOUT, E., *Rev. Sci. Instruments*, **29**, 305 (1958).

AARON L. BLUHM

POLISHES (EMULSION)

The systematic analysis of emulsion polishes is accomplished by the combined techniques of solvent extraction and infrared analysis. These products usually contain 10 to 16% non-volatile material (waxes, resins, polymers, emulsifiers, etc.) and the remainder water.

Sample Preparation for Infrared Analysis. The infrared spectrum of the

complete non-volatile portion is easily measured by depositing the film on a silver chloride disk. The following technique is recommended: Place a disk of silver chloride 25 mm in diameter and 1 mm in thickness in a die which has a cavity $1\frac{1}{2}$ " in diameter. Apply a pressure of 10,000 to 12,000 psi for two minutes, producing a thinner disk of greater diameter and consequently having better transparency. Drill two holes through the disk near the edge and directly across from each other and insert a thin steel or copper wire hook into one of the holes in such a way as to allow the disk to be suspended by the wire. Dip the disk into the test emulsion and suspend for two minutes in an oven at 110°C. Remove, allow to cool, insert the wire hook in the opposite hole and repeat the dipping and drying process until a film of sufficient thickness has been built up as indicated by testing the absorption on the spectrophotometer. An average of about 6 dips is required.

Spectra of Complete Formulations. Qualitative and rough quantitative estimations of the components of the emulsion can be made by comparison of the measured infrared spectrum with standard spectra of known materials. The first requisite of this type of analysis is the compilation of a library of spectra of waxes, resins, polymers and emulsifiers common to the formulation of emulsion polishes. Spectra of waxes, resins and emulsifiers were presented in the original paper describing this work.⁴ A very complete library of polymer spectra is given by Hummel in his work "Kunststoff, Lac und Gummi Analyse";² other collections of polymer spectra are given by Hausdorff¹ and Kagarise and Weinberger.³

The infrared spectrum of a complete polish formulation often yields information as to the type of wax present, type of emulsifier and type of polymer. The amount of information obtained from a single formulation is dependent in part on a knowledge of the technology of emulsion formulations. If the

INFRARED SPECTROPHOTOMETRY

emulsifier is a sodium soap or a borax cut resin, an absorption band at 1560 cm^{-1} will be indicative of this; if it is a morpholine emulsifier, an absorption band at 1110 cm^{-1} will be present. A pair of absorption bands at 730 cm^{-1} , 760 cm^{-1} are indicative of a wax being present. The addition of colloidal silica such as Du Pont's "Ludox" can be detected by the strong bands at 1000 to 1500 cm^{-1} and at 800 cm^{-1} which are due to silicon-oxygen bands. A strong band at 697 cm^{-1} , due to aromatic monosubstitution, generally indicates the presence of styrene.

It is often possible to make quantitative estimations of the principal components from the spectrum of the emulsion film by using the relative absorbance of the C—H deformation (or stretching) bands to compensate for variations in film thickness. For example, a method has been developed for determining the amount of ester wax present in one of the wax emulsions. The ester wax content is measured by the absorbance of the ester carbonyl at 1738 cm^{-1} , and the film thickness is corrected by the strength of the CH_2 and CH_3 deformation bands at 1468 cm^{-1} .

A similar analysis of the amount of a phenolic resin in an emulsion formula has been developed. The absorption band at 1512 cm^{-1} (benzene ring deformation) can be used to determine the per cent phenolic resin content of the formulation. The symmetric aliphatic C—H stretching band at 2830 cm^{-1} was used on samples which varied in phenolic resin content from 35 to 45%; apparently no serious error was introduced by correcting for film thickness in this manner. The results of

a series of determinations on emulsions containing known amounts of this phenolic resin are given in Table 1. The error calculated from the standard deviation is of the order of 2%. These quantitative measurements are subject to additional error if the film scatters light and thus changes shape and intensities of absorption bands. The above methods are applicable only when it is known that the emulsion does not contain waxes or other materials which have absorption bands in this area of measurement. For example, such waxes as carnauba, several IG waxes and "Duroxon R-11" have an absorption band at 1512 cm^{-1} and will interfere with the determination of the quantity of phenolic resin in an emulsion.

Complete Analysis of Emulsion Polishes. If a complete analysis of a wax emulsion is required, the components must be separated and determined quantitatively by classical methods and identified by infrared analysis. The infrared spectrum of the complete formulation will furnish sufficient information to develop an approach to the separation steps required. The first step of the separation is always that of breaking the emulsion by adding hydrochloric acid and filtering to separate the water-soluble from the water-insoluble portion. Ammonia and amine emulsifiers are recovered in the water-soluble portion as the hydrochloride salts, which can be identified by infrared characterization. Borax will be found in the water-soluble portion as boric acid and sodium chloride. Resins, waxes, polymers and fatty acids will be found in the water-insoluble portion. This material is further separated by extraction with benzene, heptane, alcohol and occasionally other solvents. The fractions are finally identified by infrared characterization. Occasionally, complete separations by solvent extraction are not possible, and it will be necessary either to resort to estimations based on infrared analysis or to complete the separation by chromatography

TABLE 1. DETERMINATION OF PHENOLIC RESIN CONTENT

Sample	Known	Infrared Detn.
1	35.0	36.5
2	37.0	38.5
3	42.0	42.0
4	45.0	45.0

on alumina or "Fluorosil." Discussion of these techniques is beyond the scope of this article.

REFERENCES

1. HAUSDORFF, H. H., "Analysis of Polymers by Infrared Spectroscopy," Perkin-Elmer Corp., Norwalk, Conn., 1951.
2. HUMMEL, DIETER, "Kunststoff, Lac und Gummi Analyse" Vols. I, II. Carl Hanser Verlag, München, Germany, 1958.
3. KAGARISE, R. E., WEINBERGER, L. A., "Infrared Spectra of Plastics and Resins," Office of Technical Services, U.S. Dept. of Commerce, PB-111.438 (1954).
4. MURPHY, J. E., SCHWEMER, W. C., "Infrared Analysis of Emulsion Polishes", *Anal. Chem.*, **30**, 116 (1958).

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POLYMERS (ESPECIALLY DIENES)

This article is concerned mainly with the determinations of the microstructures of diene polymers and of some features of the structures of α -olefin polymers. The principles involved in these determinations should be applicable to other types of polymers so that an individual discussion of each is unnecessary. The review covers the published literature on these subjects to the end of 1958.

The basic principles and methods involved in determining the composition of any mixture by infrared spectroscopy have been very well described by Brattain, Rasmussen and Cravath.¹ Basically the problem is one of solving equations of the type

$$D' = (e_1' C_1 + e_2' c_2 + e_3' c_3 + \dots) l$$

where D is the absorbance at a particular wavelength, e is the absorptivity of the components denoted by the subscripts at that wavelength, c is the concentration of the components and l is the length of light path.

There is one such equation for each component and the wavelengths are chosen so that one absorptivity (the major) is much greater than the others (the minor) at each

wavelength. White *et al.*² showed how such analyses may be made using base-line absorbances rather than true absorbances. While this was done in order to use energy recordings of spectra, the base-line method is applicable in some polymer analyses even though the recordings are made in absorbance or per cent transmission units. Robinson³ has offered further ramifications of the general method making use of differential recordings.

In applying these methods to determining the microstructures of diene polymers, i.e., the amounts of *cis*-1,4, *trans*-1,4, 1,2 and 3,4 additions in polybutadienes or polyisoprenes, the difficulty is determining the polymer absorptivity values. This arises from the fact that, except for Hevea and balata which are almost completely *cis*-1,4 and *trans*-1,4 polyisoprenes, respectively, no polymers were known which were completely 1,2 (side vinyl, $\text{CH}_2=\text{CH}$) or 3,4 (isopropenyl $\text{CH}_2=\text{C}\cdot\text{CH}_3$) or *cis*- $\text{CH}=\text{CH}$ or *trans*- $\text{CH}=\text{CH}$, as in polybutadienes. On this account the first attempts at determining the amounts of 1,2 and *trans*-1,4 additions in polybutadienes gave values which were too large since the absorptivities of pure, low molecular weight compounds of proper type (octene-1 for 1,2 addition, for example) were used.

The determination of the microstructures of polyisoprenes will be considered first although, chronologically, polybutadienes were studied earlier, since it is simpler. Richardson and Sacher⁴ developed a method for such analyses using measurements of the band at 11.9 $\text{m}\mu$ for the *cis*-1,4 and *trans*-1,4 additions, 11.25 $\text{m}\mu$ for 3,4 addition and 10.98 $\text{m}\mu$ for 1,2 addition. The *cis* and *trans* polymer absorptivities were determined from pure Hevea and balata and they showed how polymer absorptivities for the 1,2 and 3,4 additions may be obtained, starting with those for pure hydrocarbons. The basis of this method was the assumption that the integrated band intensity for each of these

structures is constant, an assumption which appears to be valid according to the work of Francis.⁵ Binder and Ransaw⁶ also discussed the analyses of polyisoprenes and showed the desirability of using bands at 8.85 μ and 8.68 μ for the *cis*-1,4 and *trans*-1,4 additions, respectively, rather than the 11.9 μ band. They also gave two other methods for determining the polymer absorptivities and showed that in ordinary emulsion or alkaline metal catalyst systems, other reactions besides simple 1,2, 1,4 or 3,4 additions must occur. These introduce other structures into the polymers and a base-line method was described to take account of the additional absorptions. Only with lithium and Ziegler type catalyst systems have polyisoprenes been produced, at the present, which are free of unusual and unknown structures.

Hampton⁷ first described a method by which the *cis*-1,4, *trans*-1,4 and 1,2 additions could be directly determined in polybutadienes. He showed how the polymer absorptivities can be determined from those of pure hydrocarbons by an iteration process involving three different polybutadienes. One of these contained a large amount of *trans*-1,4 addition (low temperature), another large 1,2 addition (sodium-catalyzed) and the third larger (20%) *cis*-1,4 addition (70–100°C emulsion). This was necessary, at the time, because no essentially pure *cis* or *trans* or 1,2-polybutadienes were available, as was the case with pure *cis* and *trans* polyisoprenes. He used a band at 13.7 μ for *cis*-1,4, 10.34 μ for *trans* 1,4 and 19.98 μ for 1,2 addition. Binder⁸ used essentially Hampton's method for analyzing polybutadienes except that, in his polymers, the *cis*-1,4 band was found at 14.7 μ . He also extended the method to analyzing butadiene-styrene copolymers and reported the analyses of a great many emulsion and sodium and potassium catalyzed polybutadienes.⁹

In all the above methods the validity of the analyses was estimated from the total found values. These are the sums of the

amounts of the various components found in the analytical polymer solution by the spectroscopic method divided by the amount of polymer known to be in the solution either by the method of preparing the solution or by determining the total solids. If the polymer contains only structures represented by the three or four components determined, and if there are no other C=C bonds present, the total found values should be 100 per cent or less and should agree with the unsaturation determined chemically. In the method for determining absorptivities the only requirement is that the major absorptivities become constant. With the advent of Ziegler type catalysts and consequently polybutadienes containing large amounts of *cis*-1,4, *trans*-1,4 or 1,2 additions, it would be unnecessary to start with absorptivities determined from pure hydrocarbons to obtain the appropriate major polymer absorptivities. Although there are references to such determinations, particularly by Natta, no details have yet been published. It should be expected that the same polymer absorptivities would apply to any type of polymer and the same test for the validity of an analysis should apply.

Smith¹⁰ described the determination of the components of mixtures of polymers. While this was concerned mainly with synthetic rubbers the method is applicable to, and has been used for, the analyses of many types of mixtures.

Another application of infrared spectroscopy is the determination of short-chain branching in polyethylenes. This has been described by Bryant¹¹ but should be compared with the work of Jones *et al.*¹² on hydrogenated polybutadienes. Theoretically the same method can be used to determine the number of CH₃ groups in other polymers but the proper calibration compounds must be used. The amounts and kinds of unsaturation in polyethylenes may be determined as for polybutadienes but great care must be exercised and calibrations must be made for films.

Infrared spectroscopy has been used to determine relative crystallinities in polypropylenes and polyethylenes. In principle it should be possible to determine absolute values, for some polymers at least, but, practically, the intensities of the crystallization bands depend markedly upon the treatment of the sample. Hence the error in such determinations may be large even though attempts are made to treat all of the samples in exactly the same manner.

REFERENCES

1. BRATTAIN, R. R., RASMUSSEN, R. S., AND CRAVATH, A. M., *J. Appl. Phys.*, **14**, 418 (1943).
2. HEIGL, J. J., BELL, M. F., AND WHITE, J. U., *Anal. Chem.*, **19**, 293 (1947).
3. ROBINSON, D. Z., *Anal. Chem.*, **24**, 619 (1952).
4. RICHARDSON, W. S. AND SACHER, A., *J. Pol. Sci.*, **10**, 353 (1953).
5. FRANCIS, S. A., *J. Chem. Phys.*, **18**, 861 (1950).
6. BINDER, J. L. AND RANSAW, H. C., *Anal. Chem.*, **29**, 503 (1957).
7. HAMPTON, R. R., *Anal. Chem.*, **21**, 923 (1949).
8. BINDER, J. L., *Anal. Chem.*, **26**, 1877 (1954).
9. BINDER, J. L., *Ind. Eng. Chem.*, **46**, 1727 (1954).
10. DINSMORE, H. L. AND SMITH, D. C., *Anal. Chem.*, **20**, 11 (1948).
11. BRYANT, W. M. D. AND VOTER, R. C., *J. Am. Chem. Soc.*, **75**, 6113 (1953).
12. JONES, R. V., MOBERLY, C. W., AND REYNOLDS, W. B., *Ind. Eng. Chem.*, **45**, 1117 (1953).

JOHN L. BINDER

POLYMERS: THEORY AND INTERPRETATION OF SPECTRA

Infrared spectroscopic studies of high polymers have been undertaken from primarily two points of view: first, for the purpose of identification and quantitative estimation of certain characteristic groups in the molecule, and second, in order to arrive at as detailed as possible an interpretation of the entire spectrum. The first approach depends on the utilization of empirical correlations derived from studies of smaller molecules containing similar groups. These correlations

have been extensively investigated,^{1, 8} and form the basis for the analytical applications of infrared spectroscopy. The second approach, which is the topic of this article, has been developing in recent years, and is motivated by the realization that deeper insights into polymer structure and forces can result from a more complete understanding of the spectrum. The methods required to achieve such detailed assignments of the spectrum of a polymer are in general not new; their concerted application to this problem is what constitutes the change in approach. We will be concerned here with outlining the various aspects of this approach, and demonstrating their application to the analysis of the spectrum of polyethylene. For a more detailed discussion of the topics covered and applications to the spectra of other polymers, reference is made to a recent review article.⁴

The theory underlying the origin of the spectra of large molecules is, of course, no different from that which holds for smaller molecules.^{2, 5} The difficulty in the spectral analysis of high polymers arises from the complexity of the system: for example, the large number of atoms, even in the repeat unit, usually makes it difficult to solve the secular equation of the normal vibration analysis. Thus, a detailed prediction concerning the forms and the frequencies of the normal modes is not available as a guide in the analysis. It was therefore natural to base early infrared studies of complex molecules on group frequencies. These are absorption frequencies which are characteristic of the vibrations of certain groups of atoms (e.g., OH, CH₂, CH₃, C=C, etc.), so that absorption in a relatively narrow spectral region can in general be associated with the presence of a particular group in the molecule. This approximation is generally valid when the motions involve groups containing light atoms (such as H) or strong bonds (double or triple bonds). However, since the form and frequency of such group modes is also often sensitive to the environment, the com-

plete dependence on a group frequency analysis can often lead to the loss of significant information contained in the spectrum. While the kind of unique interpretation that is usually possible in the study of small molecules has not been achieved in the spectral analysis of high polymers, recent work has resulted in the realization of a more detailed understanding of polymer spectra than would be possible from the group frequency approach alone. This has been a consequence of certain developments in the theoretical and experimental aspects of the analysis of macromolecules.

The mechanism of effecting a spectral analysis involves two main steps: (1) a prediction of the spectrum to be expected for a given polymer chain structure, and (2) an assignment of the observed bands to the predicted modes of vibration. The depth of the first part of the analysis will determine the extent of information that can be derived from the spectrum, while the demonstration of satisfactory agreement between observed and predicted spectrum provides the justification for the assumptions about structure and forces which were made. It is in this way, for example, that a spectral analysis can lead to structural information about the polymer. The preliminary predictive step involves the application of two theoretical techniques: a symmetry analysis and a normal vibration analysis. We consider each of these in turn.

When a molecule possesses symmetry it is possible to make many predictions about the nature of its spectrum without any additional knowledge about the molecule. By symmetry we mean that there are physical operations (such as a mirror plane or a rotation axis) which, when performed on the molecule, return it to a configuration indistinguishable from the original one. The technique for obtaining this information involves the use of group theory, and while its application has been extensive in the study of small molecules, its use in the analysis of

high polymer spectra is relatively recent. For details on the technique, reference is made elsewhere⁴; here we will quote only the results. Consider the planar zigzag chain structure of polyethylene, $(\text{CH}_2)_n$. The crystal structure is shown in Figure 1 with its associated symmetry elements. These define a group, in the mathematical sense, and by applying the methods of group theory we can obtain what is known as a character table, shown in Table 1. This character table tells us several things. First, it indicates that the vibrational modes can be divided into different species (A_g , B_{1g} , B_{2g} , etc.), which are characterized by the behavior of the vibration with respect to the various symmetry elements (+1 indicates that the vibration is symmetric with respect to the symmetry element in question, -1 that it is antisymmetric). Second, it gives the total number of modes (n_i) that will be found in each species, and how these are subdivided into pure translations of the chain (T), and translatory (T'), rotatory (R'), and internal (n_i') modes of the component (CH_2) groups. Third, it provides selection rules, i.e., information on whether modes in a given species can give rise to infrared absorption or Raman scattering. In the former case it also permits predictions as to the dichroic characteristics of the bands, which will be observable in suitably oriented specimens. Fourth, it enables the deduction of the activity characteristics of overtone and combination bands. Finally, it is frequently possible to infer, with the help of the character table, the symmetry modes of the chain, i.e., a set of vibrations which satisfy the symmetry characteristics of the various species. The actual normal modes of vibration, which strictly speaking are combinations of symmetry modes within a species, are often closely approximated by the symmetry modes themselves. Possible modes of this kind for polyethylene are shown in Figure 2. It will be noted that the analysis predicts the possible splitting of several chain modes in

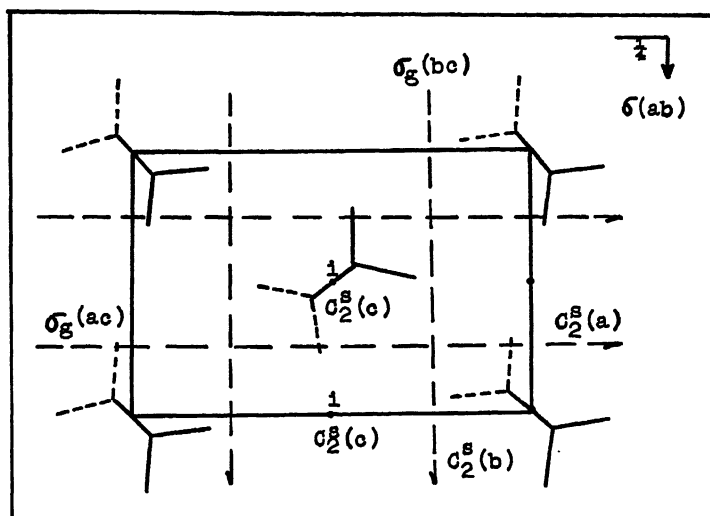


FIG. 1. Structure of crystalline polyethylene: cross section of unit cell perpendicular to chain axis

(—) represents —C— (group). σ : mirror plane, σ_g : glide plane, C_2 : two-fold rotation axis, C_2' : two-fold screw axis, i : center of inversion.

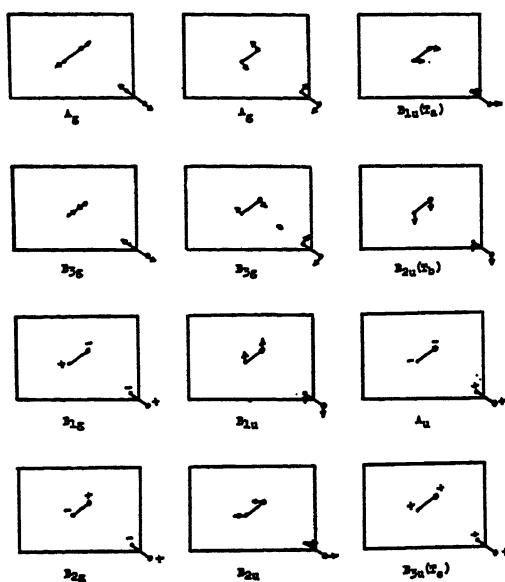
TABLE 1. CHARACTER TABLE AND SELECTION RULES FOR CRYSTALLINE POLYETHYLENE

D_{2h}	E	$C_2^s(a)$	$C_2^s(b)$	$C_2^s(c)$	i	$\sigma_g(bc)$	$\sigma_g(ac)$	$\sigma_g(ab)$	n_i	T	T'	R'	n_i'	IR	R
A_g	1	1	1	1	1	1	1	1	6	0	2	1	3	f	P
B_{1g}	1	1	-1	-1	1	1	-1	-1	3	0	1	2	0	f	D
B_{2g}	1	-1	1	-1	1	-1	1	-1	3	0	1	2	0	f	D
B_{3g}	1	-1	-1	1	1	-1	-1	1	6	0	2	1	3	f	D
A_u	1	1	1	1	-1	-1	-1	-1	3	0	1	2	0	f	f
B_{1u}	1	1	-1	-1	-1	-1	1	1	6	T_a	1	1	3	a	f
B_{2u}	1	-1	1	-1	-1	1	-1	1	6	T_b	1	1	3	a	f
B_{3u}	1	-1	-1	1	-1	1	1	-1	3	T_c	0	2	0	a	f

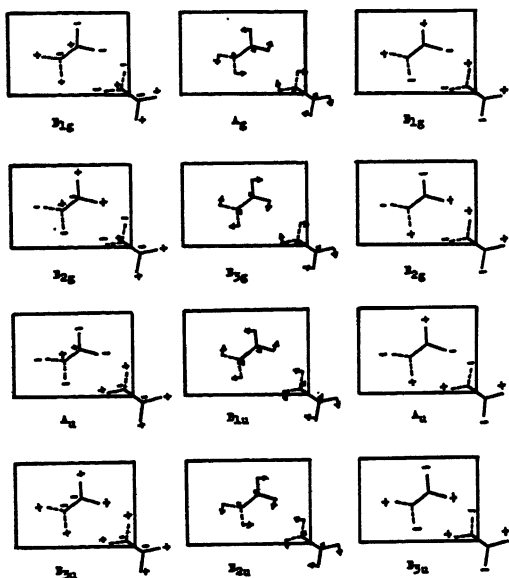
the crystal. For example, two CH_2 rocking modes are predicted (the B_{1u} and B_{2u} modes in the middle column of Figure 2b), with motions on the two chains being in-phase and out-of-phase with each other, and if the interactions between the two chains are large enough these two modes should occur at slightly different frequencies. We see, therefore, that without further knowledge of the molecule a symmetry analysis permits significant predictions to be made about the

nature of the spectrum which is to be expected.

Further information on the predicted spectrum can be derived from a normal vibration analysis. The solution of the secular equation, with the use of the appropriate force constants, can give the forms and frequencies of the normal modes, and thus provide an important guide for the assignments. Although several such calculations have been made for polyethylene, the results do not

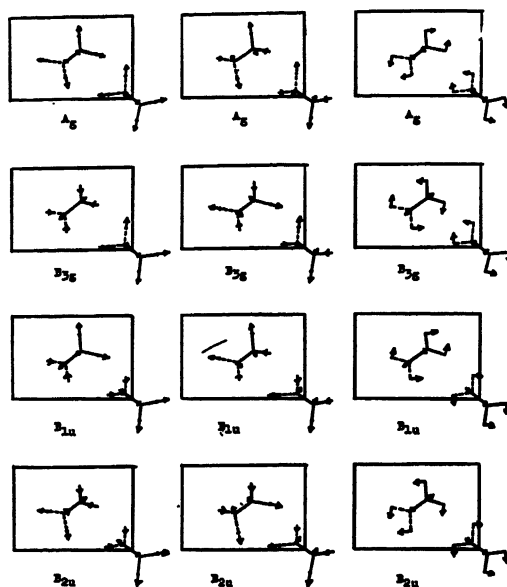


a.



b.

seem to be uniformly successful (see ref. 4 for details). Most of the modes are satisfactorily predicted, but in view of recent assignments, others are not. Polyethylene is the only polymer for which such detailed computations



c.

FIG. 2. Symmetry modes of the polyethylene unit cell. a) T and T' modes, b) R' modes, c) n_4' modes.

have been undertaken, so it is evident that this aspect of the spectral analysis of high polymers is in great need of additional attention. As an example of its utility, we may note that computations of the two polyethylene chain skeletal modes predict their frequencies at 1065 cm^{-1} , for the A_g , B_{2g} mode, and 1135 cm^{-1} , for the B_{1g} , B_{2g} mode (see Figure 2a); the observed Raman bands are found at 1061 cm^{-1} and 1131 cm^{-1} , respectively. The computations, therefore, can provide a firm base for making band assignments.

In the absence of such detailed normal vibration calculations we must depend more heavily on various experimental techniques for help in making assignments. Most of these techniques have been available for quite some time. It is only relatively recently, however, that it has been realized that through their combined use a more detailed understanding of the spectrum can

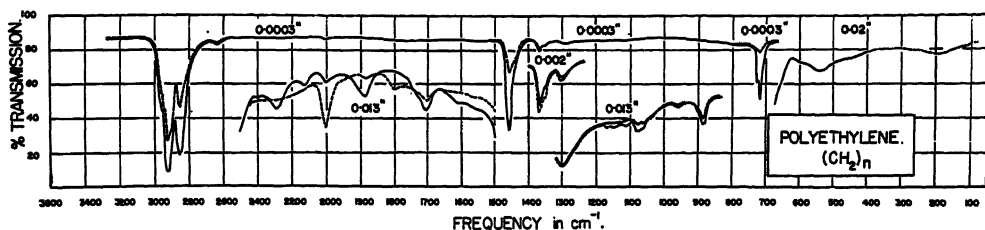


Fig. 3. Infrared spectrum of an oriented sample of (low crystallinity) polyethylene. —: radiation with electric vector polarized perpendicular to stretching direction; ---: radiation with electric vector polarized parallel to stretching direction.

emerge. We consider these several techniques below.

A prime requirement for making a detailed spectral assignment is the existence of complete spectral data. Until recently these data were not generally available. Infrared spectra were usually obtained only down to about 650 cm^{-1} , whereas significant information is often present down to 100 cm^{-1} . Increased development of prism materials transparent in the far infrared and the use of grating spectrometers have resulted recently in more extensive studies in the low frequency region. In the case of polyethylene there is not much absorption below 500 cm^{-1} (see Figure 3), but this is not true of other polymers (see ref. 4). Raman spectra of polymers are exceedingly meager, even though such data are very important. As can be seen from Table 1, some modes do not exhibit infrared activity although they are expected to be Raman active. This will always be true when the molecule possesses a center of symmetry. Thus, both low frequency infrared spectra and Raman spectra are important prerequisites to a complete spectral analysis.

The ability to identify bands with particular vibrational modes is the essential feature of making a spectral assignment. In the absence of detailed normal vibration calculations the group frequency approach can often be a useful guide, since it identifies certain regions of absorption with the vibrations of particular chemical groups. It frequently happens, however, that different group vibrations give rise to absorption in the same

region, and it is then necessary to have a more accurate method for identifying the bands. Studies of deuterated polymers provide such a means for identifying hydrogen frequencies, which of course usually constitute a significant fraction of the vibrational modes of the chain. Since the force constants do not change when deuterium is substituted for hydrogen, we expect the frequencies of those modes associated primarily with the motion of hydrogen atoms to be lowered, roughly by $\sqrt{2}$. Thus, the shift of a band on deuteration serves to identify it as originating in a hydrogen mode. In addition to such qualitative arguments, it has recently been shown⁴ that under certain circumstances it is possible to use the frequency shift ratio to identify the actual mode involved. Thus, it can be shown that for an isolated CH_2 group the frequency shift ratios for the various modes should be as follows: ν_s (symmetric stretching) and γ_t (rocking) — 1.379, ν_a (asymmetric stretching) and δ (bending) — 1.349, γ_w (wagging) — 1.323, and γ_t (twisting) — 1.414. In cases where the CH_2 modes are relatively isolated from those of the rest of the molecule these ratios should be closely reproduced. When this condition is not satisfied, as will probably be true in most cases, the numerical values will not be reproduced, but it is to be expected, and it seems to be found that the relative ratios for the various modes will be in the order indicated. Thus, deuteration studies can serve not only to identify hydrogen

modes but can be of help in the assignment of specific vibrations.

Another important tool in making assignments is the use of polarized infrared radiation in studying the spectra of oriented polymer specimens. In order for a vibrational mode to give rise to infrared absorption it is not only necessary that there be a changing dipole moment in the molecule during the vibration, but the electric field of the incident radiation must have a component along the direction of this molecular transition moment. Therefore, if polymer molecules are oriented by stretching or rolling a specimen, and spectra obtained with the electric vector alternately parallel and perpendicular to the stretching direction, it becomes possible to determine the transition moment direction associated with the various absorption bands. This information is of use in helping to identify the modes corresponding to these bands. For example, it will be seen from Table 1 that B_{3u} modes are expected to exhibit parallel dichroism, i.e., maximum absorption when the electric vector is parallel to the direction of the chain axis (which for a stretched specimen corresponds to the stretching direction). Thus, bands of crystalline polyethylene having this dichroism are identified as B_{3u} modes. Even in polymers which do not have high symmetry it is usually possible to infer the transition moment directions with respect to the chain axis of the various modes, and therefore to use the polarized spectrum as an aid in the identification of bands. When three mutually perpendicular transition moments can be associated with the vibrations of a group (which is probably the case, for example, for the CH_2 group), it is possible to specify the permitted combinations of dichroisms of the absorption bands. These are $\pi\pi\sigma$, $\sigma\sigma\pi$, $\pi\sigma u$, and uuu (π = parallel, σ = perpendicular, u = unpolarized). Thus, if the assignments of two of the modes are quite certain, their polarizations can define the expected dichroism of the third mode, and thereby assist in its as-

signment. In addition to qualitative information of the above type, quantitative values of the dichroic ratio can be used to obtain information on the distribution of transition moments in an oriented specimen. For details, see ref. 4. Polarized spectroscopic studies, therefore, are an important aspect of any attempt to arrive at detailed assignments of a polymer spectrum.

Finally, it may be necessary to examine a wide variety of specimens in order to understand better the spectrum of a polymer. If the polymer contains any impurities such as solvents or plasticizers, then the spectra of the latter must be known in order to subtract their effect from the observed spectrum. Most polymers contain a mixture of crystalline and amorphous molecules. Because of the difference in symmetry and/or structure (rotationally isomeric forms of the chain) the spectra of these two components can be different. It is therefore necessary to know from which phase a band originates. This can be ascertained by preparing polymer samples of varying crystallinity and noting the variations in band intensity, or by examining the spectrum of a melted specimen (as an analogue for the amorphous material) or of a low molecular weight crystalline analogue compound (to give the spectrum of pure crystalline material). As an example of the latter, the n -paraffins serve very well in a spectral study of polyethylene. They provide an additional advantage, viz., it is usually possible to obtain single crystals of such compounds, so that many of the features of the crystalline spectrum can be examined in more detail than is possible in an oriented polymer specimen (where the order is always of a lower degree than that of a single crystal). In addition, interchain interaction effects can be more easily studied by means of the technique of preparing solid solutions of the normal and the deuterated molecule. Each case usually presents its individual problems of this kind, but the study of such varied specimens is an important means of obtain-

POLYMERS: THEORY AND INTERPRETATION OF SPECTRA

TABLE 2. VIBRATIONAL SPECTRUM OF POLYETHYLENE

Frequency cm^{-1}		Description*			Assignment†
IR	R	R. I.	Pol'n	Phase	
~200		vw			
~430		vvw			
540-560		w			
573		w	π		
~600		w			$\text{RCH}=\text{CH}_2$
720		vs	σ_b	C,A	$\gamma_r(\text{CH}_2)(\text{B}_{2u})$; $\gamma_r(\text{CH}_2)\text{-t}$
731		vs	σ_a	C	$\gamma_r(\text{CH}_2)(\text{B}_{1u})$
888		vw	σ		$\text{RR}'\text{C}=\text{CH}_2$
890		vvw	π		$\gamma_r(\text{CH}_2)$
908		m	σ	A,C	$\text{RCH}=\text{CH}_2$
964		vvw	σ	A	$\left\{ \begin{array}{l} \gamma_r(\text{CH}_2)\text{-g} \\ \text{trans RCH}=\text{CHR}' \end{array} \right.$
990		w	σ	A,C	$\text{RCH}=\text{CH}_2$
1050		vw	π	C	$\gamma_t(\text{CH}_2)(\text{B}_{2u})$
	1061	m			$\nu_+(0)(\text{A}_g)$
1065		vw	σ		$\nu_+(0)\text{-amorphous (?)}$
1078		vw	σ	A	$\nu(\text{C}-\text{C})\text{-t,g}$
1110		vvw	π		
1131		vvw	π		$\nu_+(\pi)\text{-amorphous (?)}$
	1131	m			$\nu_+(\pi)(\text{B}_{2g})$
1150		vvw	π		
	1168	vw			$\gamma_r(\text{CH}_2)(\text{A}_g)$
1170		vvw	σ		$\gamma_r(\text{CH}_2)(\text{A}_g)\text{-amorphous (?)}$
1176		vw	π	C	$\gamma_w(\text{CH}_2)(\text{B}_{2u})$
1185		vvw	σ		
	1295	s			$\gamma_t(\text{CH}_2)(\text{B}_{2g})$
1303		w	π	A	$\gamma_t(\text{CH}_2)\text{-g}$
1353		m	π	A	$\gamma_w(\text{CH}_2)\text{-g}$
1369		m	π	A,C(?)	$\gamma_w(\text{CH}_2)\text{-g,t(?)}$
1375		w-m	$\pi(?)$	A	$\delta_s(\text{CH}_2)$
	1415	w			$\gamma_w(\text{CH}_2)(\text{B}_{2g})$
1436		vw			$\delta(\text{CH}_2)(\text{A}_g)\text{-amorphous (?)}$
	1440	m			$\delta(\text{CH}_2)(\text{A}_g)$
1457		vvw			$\delta_a(\text{CH}_2)$
1463		vs	σ_b	C,A	$\delta(\text{CH}_2)(\text{B}_{2u})$; $\delta(\text{CH}_2)\text{-t,g}$
	1464	w,b			$2 \times \gamma_r(\text{B}_{1u}) = 1462 (\text{A}_g)$
1473		vs	σ_a	C	$\delta(\text{CH}_2)(\text{B}_{1u})$
1588		vvw	σ	C	$1050 + 540 = 1590 (?)$
1640		vw	π	A,C	$\nu(\text{C}=\text{C})$
1710		vw	π		$1168 + 540 = 1708 (?)$
1722		vw	σ		$\nu(\text{C}=\text{O})$
1737		vvw			$\nu(\text{C}=\text{O})$
~1805		vw	π	A,C	$\left\{ \begin{array}{l} \nu(1078) + \gamma_r(720) = 1798 \\ 2 \times 908 = 1816 \end{array} \right.$
1894		w	σ	C	$\gamma_r(\text{A}_g) + \gamma_r(\text{B}_{1u}) = 1899 (\text{B}_{1u})$
1960		vvw	$\pi(?)$		$2 \times 990 = 1980$
					$\left\{ \begin{array}{l} \gamma_t(\text{B}_{2g}) + \gamma_r(\text{B}_{1u}) = 2026 (\text{B}_{2u}) \\ \gamma_t(1303) + \gamma_r(720) = 2023 \end{array} \right.$
2016		w	π	C,A	

TABLE 2—Continued

Frequency cm ⁻¹		Description*			Assignment†
IR	R	R. I.	Pol'n	Phase	
2144		vw	σ	C,A	$\delta(A_g) + \gamma_r(B_{2u}) = 2160 (B_{2u})$ $2 \times \nu(1078) = 2156$
2221		vw	π		$\gamma_r(A_g) + \gamma_t(B_{3u}) = 2218 (B_{3u})$
2242		vw	π	C	$\gamma_w(B_{3u}) + \nu_+(0)(A_g) = 2237 (B_{3u})$
2290		vw	σ	C	$\gamma_w(B_{3u}) + \nu_+(\pi)(B_{2g}) = 2307 (B_{1u})$ $\gamma_w(1369) + \gamma_r(964) = 2333$
2328		w	σ		$2 \times \gamma_r(1168) = 2336$
2345		w	σ	C,A	$\gamma_t(B_{2g}) + \gamma_t(B_{3u}) = 2345 (B_{1u})$
2415		vw	σ	A,C	$\nu(1078) + \gamma_w(1353) = 2431$ $\gamma_r(964) + \delta(1463) = 2427$
2473		vvw	σ	C,A	$\gamma_t(B_{2g}) + \gamma_w(B_{3u}) = 2471 (B_{1u})$ $\gamma_r(1168) + \gamma_t(1303) = 2471$ $\nu(1078) + \delta(1440) = 2518$
2525		vw	π		$\gamma_r(1168) + \gamma_w(1353) = 2521$ $\gamma_r(1168) + \gamma_w(1369) = 2537$
2549		vvw	σ		$\nu(1078) + \delta(1463) = 2541$
2597		vvw	σ(?)		$\gamma_w(B_{2g}) + \gamma_w(B_{3u}) = 2591 (B_{1u})$
2619		vvw	π		$\delta(A_g) + \gamma_w(B_{3u}) = 2616 (B_{3u})$
2635		w	σ	C	$\gamma_r(A_g) + \delta(B_{1u}) = 2641 (B_{1u})$
2658		w	σ	A	$\gamma_w(1353) + \gamma_t(1303) = 2656$
2677		vvw	π(?)		$\gamma_w(1369) + \gamma_t(1303) = 2672$
2713		vvw			$2 \times \gamma_w(1353) = 2706$
	2720	vvw,b			$\gamma_t(B_{2g}) + \delta(A_g) = 2735 (B_{2g})$ $2 \times \gamma_w(1369) = 2738$ $\delta(1440) + \gamma_t(1303) = 2743$
2741		vvw	σ		$\nu_s(CH_2)(A_g)$
	2848	vs,b			$\nu_s(CH_2)(B_{1u}); \nu_s(CH_2)-t,g$
2850		vvs	σ _a	A,C	$\nu_s(CH_2)(B_{2u})$
2857		vvs	σ _b		$\nu_s(CH_2)$
2874		w		A	$\nu_s(CH_2)(A_g)$
	2883	vvs			$\nu_s(CH_2)(B_{2u})$
2899		vvs	σ _b	C	$\delta(A_g) + 2 \times \gamma_r(B_{1u}) = 2902 (A_g)$ $2 \times \delta(B_{2u}) = 2926 (A_g)$
	2912	w			$\nu_s(CH_2)(B_{1u}); \nu_s(CH_2)-t,g$
2924		vvs	σ _a	A,C	$\delta(B_{1u}) + \delta(B_{2u}) = 2936 (B_{2g})$
	2932	w			$\nu_s(CH_2)$
2960		w			$\gamma_t(B_{2g}) + \nu_+(0)(A_g) + \gamma_r(B_{1u}) = 3087 (B_{3u})$
3080		vw	π		$2 \times \nu(C=C) = 3280$
3274		vvw	π		$\nu(OH)$
3371		vvw	π	A,C	$\gamma_w(B_{2g}) + \gamma_t(B_{2g}) + \gamma_r(B_{1u,2u}) = 3436 (B_{1u,2u})$
3433		vvw	σ		$\nu_s(A_g) + \gamma_r(B_{1u}) = 3614 (B_{1u})$ $\nu_s(2883) + \gamma_r(720) = 3603$
3605		w	σ	C,A	$2 \times \gamma_t(A_g) + \gamma_t(B_{3u}) = 3640 (B_{3u})$
3648		w	π		$\delta(B_{1u}) + \nu_+(\pi)(B_{2g}) + \nu_+(0)(A_g) = 3665 (B_{3u})$
~3700		vvw	π(?)		$\gamma_w(B_{2g}) + \gamma_w(B_{3u}) + \nu_+(\pi)(B_{2g}) = 3722 (B_{3u})$
3810		vvw	σ		$2 \times \gamma_r(A_g) + \delta(B_{1u}) = 3809 (B_{1u})$
3876		vvw	σ		$\delta(B_{2u}) + \gamma_t(B_{2g}) + \nu_+(\pi)(B_{2g}) = 3889 (B_{2u})$

TABLE 2—Continued

Frequency, cm ⁻¹		Description*			Assignment†
IR	R	R.I.	Pol'n	Phase	
3900		vw	π		$\nu_s(A_g) + \gamma_t(B_{3u}) = 3998 (B_{3u})$
3982		vw	σ		$\nu_s(B_{1u}) + \nu_+(0)(A_g) = 3985 (B_{1u})$
3989		vw	π		$\nu_s(B_{1u}) + \nu_+(\pi)(B_{2g}) = 3981 (B_{3u})$
4027		vw	σ		$\nu_s(B_{2u}) + \gamma_r(A_g) = 4025 (B_{2u})$
4055		vw	π		$\left\{ \begin{array}{l} \nu_s(B_{1u}) + \nu_+(\pi)(B_{2g}) = 4055 (B_{3u}) \\ \nu_s(A_g) + \gamma_w(B_{3u}) = 4059 (B_{3u}) \end{array} \right.$
4106		w	σ		$\nu_s(B_{1u}) + \gamma_r(A_g) = 4092 (B_{1u})$
4185		w	σ		$\nu_s(2883) + \gamma_t(1303) = 4186$
4221		w	π		$\nu_s(B_{1u}) + \gamma_t(B_{2g}) = 4219 (B_{3u})$
4255		mw	σ		$\nu_s(2883) + \gamma_w(1369) = 4252$
4327		m	σ		$\left\{ \begin{array}{l} \nu_s(A_g) + \delta(B_{1u}) = 4321 (B_{1u}) \\ \nu_s(B_{2u}) + \delta(A_g) = 4339 (B_{2u}) \\ \nu_s(A_g) + \delta(B_{2u}) = 4346 (B_{2u}) \end{array} \right.$
4629		vw	σ		$\nu_s(A_g) + \nu_+(0)(A_g) + \gamma_r(B_{1u,2u}) = 4635 (B_{1u,2u})$
4695		vw	π		$\left\{ \begin{array}{l} \nu_s(B_{2u}) + \gamma_t(B_{3u}) + \gamma_r(B_{2u}) = 4670 (B_{3u}) \\ \nu_s(B_{1u}) + \gamma_t(B_{3u}) + \gamma_r(B_{1u}) = 4705 (B_{3u}) \\ \nu_s(A_g) + \nu_+(\pi)(B_{2g}) + \gamma_r(B_{1u}) = 4710 (B_{2u}) \end{array} \right.$
4888		ms	π		$\nu_s, \nu_s(A_g) + \gamma_t(B_{2g}) + \gamma_r(B_{1u}) = 4892 (B_{3u})$
4987		w	σ		$\left\{ \begin{array}{l} \nu_s, \nu_s(B_{1u,2u}) + 2 \times \gamma_t(B_{3u}) = 4983 (B_{1u,2u}) \\ \nu_s, \nu_s(B_{1u,2u}) + 2 \times \nu_+(0)(A_g) = 5004 (B_{1u,2u}) \end{array} \right.$
5076		vw	π		$\nu_s, \nu_s(B_{1u}) + \nu_+(\pi)(B_{2g}) + \nu_+(0)(A_g) = 5079 (B_{3u})$
5107		vw	σ		$\nu_s, \nu_s(B_{2u}) + \gamma_r(A_g) + \nu_+(0)(A_g) = 5107 (B_{3u})$
5181		vw	π		$\nu_s, \nu_s(B_{1u}) + \gamma_r(A_g) + \nu_+(\pi)(B_{2g}) = 5186 (B_{3u})$
5397		vw	π		$\left\{ \begin{array}{l} \nu_s(B_{1u}) + \delta(B_{1u}) + \gamma_t(B_{3u}) = 5373 (B_{3u}) \\ \nu_s(B_{2u}) + \delta(B_{2u}) + \gamma_t(B_{3u}) = 5412 (B_{3u}) \\ \nu_s(B_{1u}) + \delta(B_{1u}) + \gamma_t(B_{3u}) = 5447 (B_{3u}) \end{array} \right.$
5453		vw	π		$\nu_s(A_g) + \delta(A_g) + \gamma_w(B_{3u}) = 5464 (B_{3u})$
5488		vw	σ		$\nu_s(A_g) + \delta(B_{1u}) + \gamma_r(A_g) = 5489 (B_{1u})$
5662		w	σ		$\nu_s(A_g) + \nu_s(B_{1u}) = 5698 (B_{1u})$
5770		m	σ		$\nu_s(A_g) + \nu_s(B_{2u}) = 5782 (B_{2u})$

* vs = very strong, m = medium, w = weak, b = broad, π = parallel, σ = perpendicular ($\sigma_{a(b)}$ = polarization along a(b) crystal axis), A = amorphous, C = crystalline.

† ν = stretching, δ = bending, γ_w = wagging, γ_t = twisting, γ_r = rocking. Amorphous chain fundamentals and combinations do not carry species designation. t = trans, g = gauche configuration.

ing information which is directly relevant to the problem of making satisfactory assignments.

As an illustration of the above techniques we will describe briefly the analysis of the spectrum of polyethylene. For the detailed arguments and references the reader is referred elsewhere.⁴ The bands observed in the infrared and Raman spectra of polyethylene are given in Table 2, together with their relative intensity, polarization, and phase of origin. The structure of polyethylene is well-

known from x-ray diffraction studies, and has been shown in Figure 1. The results of the symmetry analysis of the spectrum are contained in Table 1 and Figure 2. Normal vibration calculations have been made, and permit the satisfactory identification of most of the infrared active modes of the crystal, viz., ν_s , ν_a , δ , and γ_r . Studies on single crystals of *n*-paraffins indicate that these modes are split, as predicted, and their polarization with respect to the unit cell axes permits species assignments to be made. The

Raman fundamentals do not exhibit splitting, and it has been shown⁴ that this is to be expected and that it leads also to a unique species assignment. Some of the infrared bands are due to impurities, and these are fairly readily identified. The only two infrared active fundamentals which had not been satisfactorily assigned were $\gamma_w(\text{CH}_2)$ and $\gamma_s(\text{CH}_2)$, nor had the many weaker bands been explained in detail. It has been shown that in fact the solution of the former problem lies partly in a satisfactory assignment of these weaker overtone and combination bands, and that the new assignments, of $\gamma_w(\text{CH}_2)$ to the 1176 cm^{-1} band and $\gamma_s(\text{CH}_2)$ to the 1050 cm^{-1} band, give the most consistent explanation of the spectrum. The assignment of bands to the crystalline component then permits some reasonable conclusions to be drawn about the nature of the spectrum of amorphous polyethylene. The results of all these considerations are given in the last column of Table 2. Not all problems have been solved: if the new assignments of $\gamma_w(\text{CH}_2)$ and $\gamma_s(\text{CH}_2)$ are correct then the normal vibration calculations are in need of revision, and a satisfactory theory is yet to be developed to account for the details of the crystalline chain splittings. Nevertheless, the basic framework of a set of assignments for polyethylene appears to have been established, and with this has come a deeper understanding of the properties and behavior of this polymer.

The spectra of many other high polymers have been analyzed to a similar degree, though in most cases not in as great detail. It seems clear that when this has been achieved a new range of power in the infrared spectroscopic tool will have been demonstrated.

REFERENCES

1. BELLAMY, L. J., "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, New York, 1958.
2. HERZBERG, G., "Infrared and Raman Spectra," D. Van Nostrand Co., New York, 1945.

3. JONES, R. N. AND SANDORFF, C., in "Technique of Organic Chemistry," Vol. IX. Interscience Publishers, New York, 1956.
4. KRIMM, S., "Fortschritte der Hochpolymeren-Forschung," in press.
5. WILSON, E. B., JR., DECUS, J. C., AND CROSS, P. C., "Molecular Vibrations," McGraw-Hill Book Co., New York, 1955.

S. KRIMM

 RESOLUTION AND MIXTURE ANALYSIS
(AROMATIC AMINES)

Near-infrared spectroscopy is a valuable tool for analyzing mixtures of aromatic amines. Methods have been reported for analyzing mixtures of primary and secondary aromatic amines and mixtures of N-alkyl and N-alkyl-N-hydroxyalkyl aromatic amines.^{3,4} A discussion of these methods will illustrate the analytical potential of near-infrared spectroscopy.

Primary and Secondary Aromatic Amines. Primary aromatic amines are characterized by two relatively intense absorption bands near 1.97 and 1.49 microns. The band at 1.97 microns has been assigned to a combination of N—H bending and stretching modes and the one at 1.49 microns to the first overtone of the symmetric N—H stretching vibration.¹ Secondary amines exhibit an overtone band near 1.49 microns, but they do not absorb appreciably in the combination region. These differences in absorption, which are shown by the spectra of aniline and N-ethylaniline in Figure 1, provide the basis for rapid, quantitative analytical methods.

The analyses are normally carried out on 1% solutions in carbon tetrachloride, using 10-cm cells. Beer's law is followed under these conditions within the limits of experimental error. Although the background absorption of carbon tetrachloride solutions of amines increases with time, the net absorption of most amines remains constant for several hours. Background corrections can be obtained at two suitably located wave

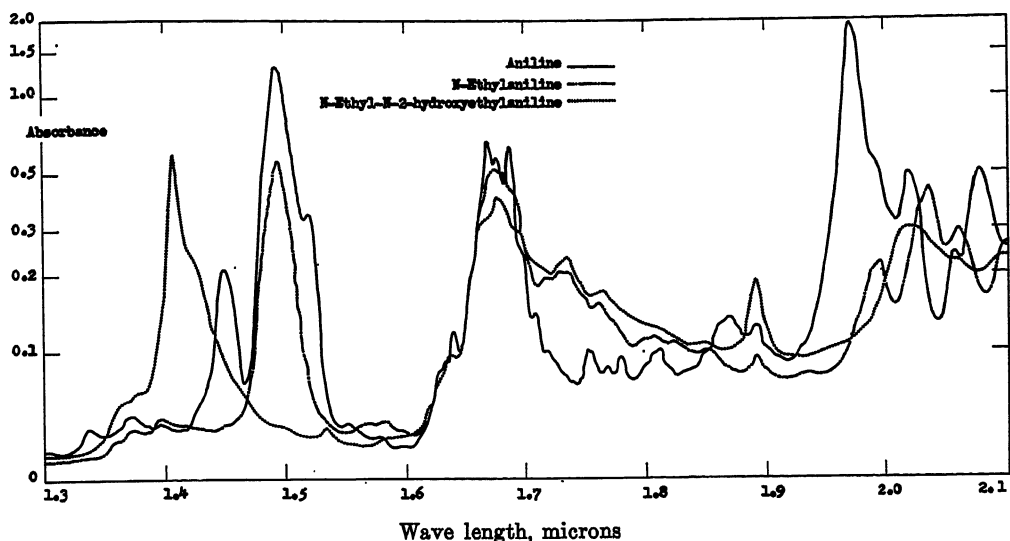


FIG. 1. Near-infrared absorption spectra of some aromatic amines (1% solutions in carbon tetrachloride; 10-cm cell.)

lengths, such as 1575 and 1915 μ . Closer attention must be given to the time variable if a strong electron-donating substituent is present, since these compounds sometimes react appreciably with the solvent. Control of the slit width is not critical if the half-intensity band width is kept less than 2 μ .

Mixtures covering practically the entire concentration range can be analyzed with standard deviations of $\pm 1\%$. Low concentrations of primary amines can be determined with greater precision by using 5 or 10% solutions of the samples and measuring only the combination band. Over this limited concentration range, the relation between net absorbance and concentration is linear, even though it is not quite the same as the one used with dilute solutions. The standard deviation for the determination of aniline in N-ethylaniline by this procedure is about $\pm 0.1\%$. Differential measurements in which a 5–10% solution of the secondary amine is used in the reference beam are also useful when the concentration of primary amine is low.

Tertiary amines do not exhibit appreciable absorption in either the 1500- or the 1975- μ

region, and thus they do not interfere with the primary and secondary amine determinations. The overtone and combination bands of aliphatic amines are shifted to about 1525 and 2000 μ , respectively. As a result, the absorption of these amines at the analytical wave lengths for the aromatic amines is weak, and the interference is not serious.

The molar absorptivities of the N—H bands vary by a factor of about 1.5, depending on the structure of the amines;^{2, 3, 5} thus, for highest accuracy, calibration data must be obtained for the particular system being studied. Approximate group-type analyses are possible, however, if the compounds involved are structurally similar.

N-Alkyl- and N-Alkyl-N-Hydroxyalkyl Aromatic Amines. Many mixtures of secondary and tertiary aromatic amines can be analyzed by conventional infrared spectroscopy. The secondary amine is usually determined from the intensity of the fundamental N—H stretching band near 3 microns. If, however, either amine contains an hydroxyl group, the O—H absorption may mask the weaker N—H band.

The first overtones of the O—H and N—H

stretching vibrations occur near 1.4 and 1.5 microns, respectively. The high resolution available with near-infrared instruments allows the two bands to be resolved easily, and with dilute solutions in carbon tetrachloride, there is little mutual interference at either wave length (Figure 1). These considerations make near-infrared spectroscopy particularly attractive for the analysis of secondary and tertiary aromatic amines when one or more of the components contain an hydroxyl group.³

These compounds can be studied conveniently as 2% solutions in carbon tetrachloride with 10-cm cells. The N—H bands obey Beer's law over the 0–2% concentration range, but the O—H bands show deviations due to intermolecular hydrogen bonding. The effects can be decreased by using more dilute solutions with longer cells, by using a more polar solvent, or by working at an elevated temperature. In practice, however, it is usually more convenient to use working curves and to maintain reasonably close temperature control than it is to attempt to eliminate hydrogen bonding. The net absorption of these amines in carbon tetrachloride remains practically constant for 24 hours, but the background absorption increases considerably with time. Suitable background corrections can be obtained from a line drawn between 1325 and 1550 $m\mu$.

Standard deviations for analyses of this type are $\pm 1\%$ or less. Low concentrations of secondary amines, however, can be determined with a standard deviation of $\pm 0.1\%$ by working with 5 or 10% solutions and measuring only the N—H band. Differential measurements can also be used to lower the detection limit for secondary amines to 0.1% or less.

Primary amines interfere seriously with the determination of secondary amines. An interfering primary amine can be determined from the absorption of its combination band near 1975 $m\mu$, however, and a correction can be applied to the secondary amine

determination. Primary amines that do not contain an hydroxyl group do not interfere with the determination of tertiary amines.

REFERENCES

1. KAYE, W., *Spectrochim. Acta*, **6**, 257 (1954).
2. LIDDEL, U. AND WULF, O. R., *J. Am. Chem. Soc.*, **55**, 3574 (1933).
3. WHETSEL, K. B., ROBERSON, W. E., AND KRELL, M. W., *Anal. Chem.*, **29**, 1006 (1957).
4. *Ibid.*, **30**, 1594 (1958).
5. *Ibid.*, **30**, 1598 (1958).

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SAMPLE PREPARATION

Cell Construction and Materials

Most work in infrared absorption spectroscopy requires the use of cells consisting of transparent windows to confine the sample and spacers or bodies to support the windows and determine the sample thickness. The choice of window material is limited by the transparency, strength, inertness, and availability of suitable substances. The alkali halides are most widely used in cell construction, particularly sodium chloride which is transparent at wavelengths as long as 16 μ and potassium bromide which can be used to 26 μ . These crystals are grown synthetically and are readily available. They can be cut to suitable size by cleaving¹ along a principal plane using a sharp instrument. Crystals prepared in this way are often of sufficiently good optical clarity to be used without additional polishing. When polishing is necessary they can be readily rough ground using fine emery and then polished on a lap dressed with a slurry of cerium oxide or "Barnsite" in ethyl alcohol.¹ The surfaces of these windows are easily fogged by exposure to atmospheric water vapor or moist samples and, although it is sometimes permissible or even desirable to use fogged or unpolished plates,² the practicing spectroscopist soon learns to repolish his damaged windows by standard or special techniques.³ Other alkali-halides are some-

times used when special properties are desired. Cesium bromide and cesium iodide are useful in the far infrared to wavelengths beyond 40 and 50 μ , respectively. However, they are very sensitive to attack by moisture. Although it is possible to waterproof rock salt by coating with selenium,⁴ usually other materials are used with moist samples or water solutions. Such substances as calcium fluoride, lithium fluoride, barium fluoride and thallium bromide-iodide are quite resistant to damage from water and can be polished^{5, 6} to give good optical surfaces. Silver chloride^{7, 8, 9} is also quite resistant to damage from water but is sensitive to the actinic action of visible light and is corrosive to the base metals. However, it can be protected by coating with stibnite, plastic, or silver sulfide.^{10, 11, 12} Alkali halide windows can be fabricated by pressing finely ground powder at elevated temperature.¹³ Such windows are inexpensive and can be discarded when damaged. Unusual window materials for special purposes include diamond,¹⁴ sapphire, arsenic trisulfide, plastics such as polytrifluorochloroethylene,¹⁵ polyethylene,^{16, 17} and "Pliofilm",¹⁸ the latter two being particularly useful in the far infrared, and quartz and special glasses for use in the near infrared.

Windows are frequently sealed to cell bodies by means of lead gaskets which have been wetted with mercury. The surface of the amalgamated lead is soft and conforms closely to the window providing a leak proof and even vacuum and pressure tight seal. For thin liquid cells the gasket serves as a spacer. Copper gaskets are also used, particularly when very thin spacers are desired. These are first treated by immersion in a solution of mercuric chloride in glacial acetic acid. The blackened surface of the gasket is wiped clean and is then amalgamated with mercury. Other useful gasket materials are indium metal and some polymers which are soft and can be made to seal with pressure alone, and silver which can be used in con-

tact with silver chloride. Low melting waxes, greases, cements, and resins such as glyptal and the epoxy resins are also widely used in cell construction. Low melting solders,¹⁹ for example those containing indium, can sometimes be used for mounting windows, and silver chloride^{20, 21, 22, 23} can be melted and used as a sealing agent.

Liquid Samples

Liquid samples are probably the easiest to handle in infrared spectroscopy. Typically, a liquid layer between 0.02 and 0.1 mm in thickness is required to produce a useful spectrum. For optimum sensitivity in quantitative analysis, the cell should be of such thickness that the band being measured transmits about thirty-seven per cent of the incident radiation.²⁴ A cell can be demountable, in which case the sample and a spacer are placed on one window, covered with another window, and the entire sandwich is clamped together (Figure 1). The spacer can be omitted in the case of very viscous samples or when extremely thin layers are required. It is not easy to assemble demountable cells with reproducible thickness because thin spacers are easily wrinkled and dust particles and sample tend to become trapped between the spacer and the window. The use of a loop of fine wire as a spacer has been found to give more reproducible cell thicknesses. Windows for demountable cells have been prepared²⁵ by etching a depression in a flat window with water or a water-alcohol mixture. Such cells require no spacer. When closely controlled thickness is necessary, as in quantitative analysis, or when the sample is too volatile to be contained in a demountable cell, a sealed cell must be used.^{26, 27, 28} These are usually constructed with amalgamated lead or copper gaskets and spacers. A convenient form of cell is provided with tapered fittings to accept hypodermic syringes for filling (Figure 1). The taper can be plugged after filling or the syringe can be left in place to

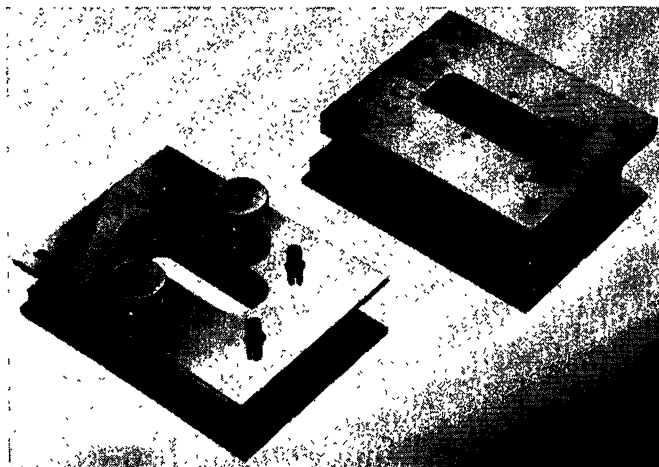


FIG. 1. A demountable infrared cell (left) and a sealed cell with fitting for syringe (right). These cells are used for liquid or solution samples.

provide a reservoir in case of leakage or evaporation. By using two syringes the sample can be readily recovered.²⁹ One type of cell, combining the features of sealed and demountable cells, is sealed with mercury by filling a groove cut in the face of the windows³⁰ or by filling a plastic bag surrounding the cell.³¹ A demountable cell with provision for sucking off escaping vapor has been devised for use with toxic liquids.³²

The thickness of thin liquid cells can be determined by taking advantage of the interference fringes observed on a spectrogram when the empty cell is placed in a spectrometer.^{33, 34, 35} Other methods of determining cell thickness are based on the use of interferometers with visible light,³⁶ weight differences with the cell filled and empty,³⁷ and intensities of absorption bands of a material previously run in a cell of known thickness.³⁸

Solutions of liquids, solids, and even gases in liquid solvents are generally studied in the same cells used for pure liquids. In cases of extremely dilute solutions with relatively transparent solvents it is often desirable to use unusually long absorption cells. Cells as long as 5 cm have been used to determine water in "Freon" refrigerants,^{39, 40, 41} impurities in titanium tetrachloride,⁴² and impuri-

ties in liquid chlorine.⁴³ Sensitivities approaching and even surpassing parts per million of some impurities have been reported. If the solvent is not sufficiently transparent to permit the use of long path lengths it is often feasible to extract the components to be determined with a transparent solvent. Oil and phenols in water have been determined in this way.⁴⁴

In most applications highly transparent solvents will not be available. Frequently a complementary pair of solvents is used over different spectral ranges. For example, carbon tetrachloride is a very useful solvent even in thick layers except where it is strongly absorbing between 12.5 and 13.5 μ , whereas carbon disulfide is useful at 13 μ , but absorbs strongly at about 4.5 and 6.5 μ . Of course, the choice of solvent is dictated by solubility as well as desirable spectroscopic properties.⁴⁵ It is sometimes possible to improve solubilities by using additives. For example, 0.5 to 2% triethylamine⁴⁶ will render such materials as acids soluble in carbon tetrachloride or carbon disulfide.

It is essential for the spectroscopist to be aware of the influence that a solvent can have on the spectrum of a solute. For example, the O-H bands of alcohols near 3 μ

shift in frequency and become weaker and sharper as hydrogen bonds are broken by dilution. Spectra of molecules which can exist in different isomeric forms due to hindered rotation about a single bond can also vary considerably with degree of dilution.

Water is an important solvent in chemistry, particularly in inorganic and biological chemistry, but unfortunately it is not a good solvent for infrared spectroscopy because of its intense absorption⁴⁷ and because of the solubility of many of the alkali halides used for cell windows. However, thin cells of appropriate window material have been used for both qualitative^{48, 49, 50, 51} and quantitative⁵² studies of aqueous solutions.

The advent of double beam spectrometers has led to the popularity of differential techniques⁵³ in which absorption bands of the solvent are "cancelled" from the spectrum of a solution by placing a cell containing pure solvent in the reference beam. Because it is necessary to match the amount of solvent present in the two beams it is desirable to have a cell of variable path length. A number of cells have been devised^{54, 55, 56, 57} using screw threads for adjustment. A much simpler but less versatile variable path cell makes use of wide windows with a wedge-shaped spacer and provision for positioning the assembly in the beam to obtain the desired thickness. In some applications^{58, 59} in which interactions between two components are to be studied it is useful to place a double cell with separate components in the reference beam and a thicker cell with components combined in the sample beam.

When the amount of sample is limited it is necessary to resort to micro sampling techniques. In its simplest form⁶⁰ this merely involves the use of a small cell of minimum cross section mounted close to an image of the monochromator slit where the beam is smallest. These cells typically require about .01 ml of sample, compared with 0.1 ml for a conventional full sized cell. A demountable

microcell has been described⁶¹ which incorporates an annular groove cut into the face of one window. Capillarity ensures that the sample will remain in the limited area defined by the groove. Further reduction in sample size requires the use of a beam-condensing device to reduce optically the size of the radiation beam as it passes through the sample. Some beam condensers⁶²⁻⁶⁷ utilize reflecting optics of the Schwarzschild type to provide a highly convergent beam forming an extremely small image. To avoid excessive heating of the sample, the condensers are usually mounted behind the exit slit of the monochromator in dispersed radiation. Hence they cannot be used in most double beam instruments. Cells for these devices can be miniature versions of conventional designs with flat windows or they can be constructed of capillary tubing of silver chloride⁶⁸ or polyethylene.⁶⁹ Cells have also been constructed by removing material from the interior of a solid window with an ultrasonic cutter.⁷⁰ Because of the small sample area involved, some liquids can even be mounted as self-supporting films in small rings.⁷¹ Samples as small as 0.1 microgram can be studied with these methods.

Lower powered beam condensers^{72, 73, 74} using refracting optics have been devised for use with microcells of more modest sample requirements of fractions of a micro-liter (Figure 2). Sample heating is less severe with these devices and they can be placed in the usual sample location of double beam instruments.

It is often desirable to raise the temperature of a sample and a number of devices have been described for this purpose. Ordinary cells can be heated with hot air blowers⁷⁵ or heat lamps or they can have attached electrically heated plates.^{76, 77} More elaborate designs have been proposed for use, for example, with corrosive materials.⁷⁸ Uses for heated cells range from studies of free energy differences of rotational isomers⁷⁹ or energy of hydrogen bonding⁸⁰ to quantitative analy-



FIG. 2. An infrared microcell for use with beam condenser. This cell has a volume of about 0.2 microliter and is filled using a capillary.

sis of mixtures which are insoluble at ordinary temperatures.⁸¹ It is possible⁸² to observe weak emission spectra from thin layers of liquid samples even at relatively low temperature (e.g. 150°C). Because most modern double beam instruments respond to all radiation passing through or originating in the sample, this presents a difficulty in the study of very hot samples. In addition, the relative intensities and band shapes of the spectra of many materials have been found to depend on temperature.^{83, 84}

The alkali halide windows used in cell construction are brittle and usually will not tolerate much pressure, but by proper cell design windows^{48, 55} can be made to stand several atmospheres of pressure. Gases which are liquefied at relatively low pressure, e.g., the butenes,⁸⁶ can then be studied in the liquid phase at room temperature. In studies of the properties of materials under extremely high pressure, thick windows of sodium chloride,^{87, 88} calcium fluoride,⁸⁷ syn-

thetic sapphire^{89, 90, 91, 92} and diamond¹⁴ have been used at pressures up to 200,000 atmospheres.⁸⁸

Liquids are usually considered to be isotropic in structure. Under certain conditions, however, a definite orientation can be induced in some liquids. For example, streaming dichroism can be observed, using polarized radiation to observe flowing polymer solutions.^{93, 94} Another form of induced orientation is the electro-optic Kerr effect which has been observed for nitrobenzene.⁹⁵ Optical rotatory dispersion has also been studied in the infrared for a few compounds.⁹⁶

The refractive index of liquids can be determined in the infrared region by measuring the shift of the interference fringes when a cell with highly reflecting windows (e.g., germanium) is filled with the sample to be studied,⁹⁷ or by measuring the critical angle.^{98, 99} Refractive index can also be determined using a hollow prism filled with a liquid sample.^{100, 101, 102}

It is sometimes necessary to alter the form of difficult samples in order to obtain infrared spectra. A technique of this type often completely changes the structure of the compound but if it is a reproducible change the approach is still useful for analytical purposes. One such method is to pyrolyze the sample and study the liquid residue.^{103, 104, 105} This technique has been useful even for quantitative analysis of difficult mixed polymers.^{106, 107}

Gaseous Samples

The simplest cell for use with gas samples is a glass or metal cylinder, usually about 10 cm in length, closed at both ends with suitable windows (Figure 3). To improve sampling efficiency the cell body is sometimes tapered to conform to the shape of the radiation beam.¹⁰⁸ A demountable type gas cell¹⁰⁹ can be constructed by using a large diameter glass standard taper joint instead of the usual body. Cell windows can be mounted

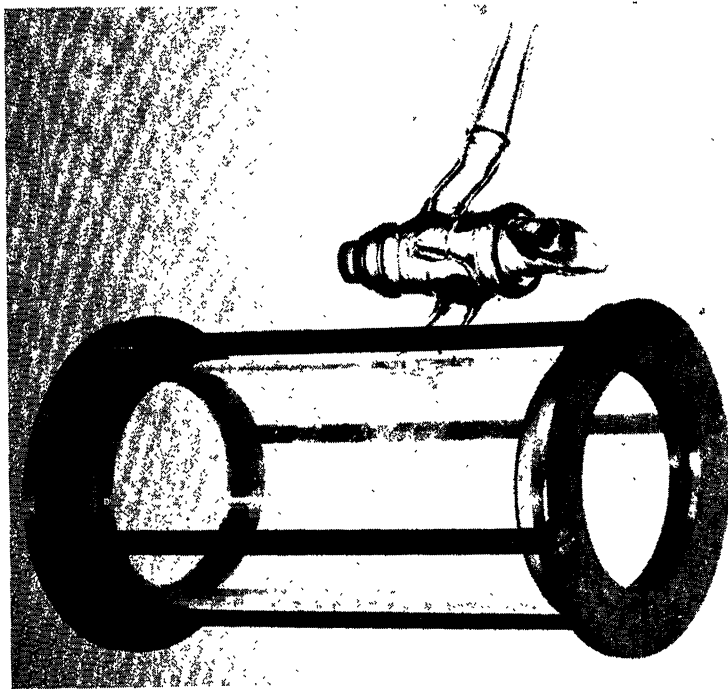


FIG. 3. A 10-cm cell for infrared study of gases.

with amalgamated lead or copper spacers, wax, grease, gaskets of soft metal or polymer, melted silver chloride or metallic solder. Provision for evacuating and filling the cell must be provided, usually through a stopcock or needle valve. Special arrangements are required for the evacuation of cells using thin plastic windows such as polyethylene. Some workers¹⁸ have reinforced the windows with wire grids at the expense of lost energy. Others¹⁷ use solid metal end plates held in contact with the windows while the cell is evacuated. The cell is pressurized to one atmosphere with a transparent gas before removing the plates. Special cells have been devised for corrosive gases such as HCl and HF.¹¹⁰

There is a serious problem associated with the infrared study of dilute or weakly absorbing gas samples. It is often necessary to provide long absorbing paths in order to have a sufficient number of molecules in the beam. This can be done by separating the

spectrometer source from the monochromator by the desirable distance and either collimating the radiation through a cell or using a light-pipe cell. But this is an extravagant use of space and sample, which is not often tolerable. It is possible to fold long optical paths into smaller volumes by multiple reflection and a number of such folded path cells have been devised¹¹¹⁻¹¹⁹ (Figure 4). These cells have been particularly useful in studies of natural¹¹⁹ and polluted atmospheres¹¹⁷ and in the determination of impurities in oxygen. If sampling efficiency is expressed as path length per volume of sample, the ordinary folded path cell with a path length of 10 meters can be made perhaps five times more efficient than a typical 10-centimeter cell. An additional tenfold increase in sampling efficiency can be obtained with a miniature folded path cell used in conjunction with a beam condensing device¹²⁰ (Figure 5). Another approach, in contrast with the use of long path lengths,

INFRARED SPECTROPHOTOMETRY



FIG. 4. A multi-pass gas cell mounted on a spectrophotometer. This cell has a maximum path length of 10 meters folded into a space 4.5 liters in volume.

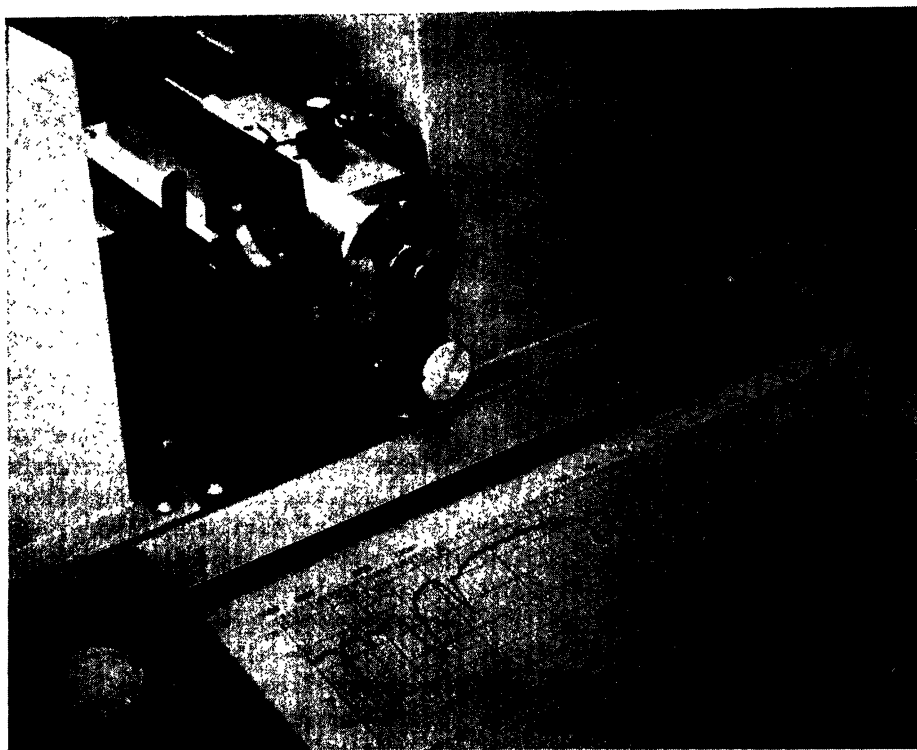


FIG. 5. A multi-pass micro-cell for study of small amounts of gases. This cell has a volume of 22 ml and a path length of 60 cm, and is used with a beam condenser.

is to concentrate the molecules into a reduced volume. This can be done by condensing the sample at low temperature onto a cold window,¹²¹ by compressing the gas into a small volume¹²² or even liquefying the gas by compression,^{48, 85} or by dissolving the gas in a suitable liquid solvent.^{123, 124}

Just as compounds which are normally gaseous can be studied as liquids or solids at reduced temperature, liquids and solids can be vaporized at elevated temperatures and studied as gaseous samples. A number of cells have been described for this purpose,^{125, 126} including some folded-path cells^{111, 116} and some cells can be cooled as well as heated.^{127, 128} Variable temperature gas cells have been used, for example in the study of rotational isomerism of 1,2-dibromoethane¹²⁵ and the thermal decomposition of *n*-butane at 280°C¹²⁹ and ethylene oxide at 410–470°C.¹³⁰ At the higher temperatures infrared emission spectra are observable. The emission spectrum of B₂O₃ vapor at 1700°K has been studied¹³¹ by placing the material in an open "Alundum" tube. Study of the emission and absorption of flames can provide information on the nature of intermediate and unstable chemical species^{132, 133} and on the temperature of the flame. In some cases a rapid-scanning spectrometer with cathode ray tube presentation of the spectra has been used to follow the course of fast reactions.¹³⁴ Emission spectra from gases have also been excited by means of radio-frequency discharges.^{135, 136}

In order to make satisfactory quantitative measurements of gaseous samples, certain special precautions are necessary. In the preparation of standardizing mixtures by pressure measurement proper attention must be given to the influence of temperature and gas-law deviations. A weighing pipette method has been devised for use with ether-alcohol¹³⁷ mixtures and a cell filling technique using volume metering has been described.¹³⁸ It is necessary to ensure thorough mixing of gaseous samples, and a gas cell with an

integral agitating system can be used to accomplish this.¹³⁹ Finally, it must be recognized that large deviations from Beer's law often occur in gaseous systems because of pressure broadening effects.¹⁴⁰ Multi-component gas analysis can become quite difficult because the extent of the broadening depends on the constituents present and their partial pressures. Because of this, and also because most analytical spectrophotometers have insufficient resolution to give an accurate measure of the intensities of the very sharp lines of light gases, it has become commonplace to pressure broaden spectra intentionally by adding a high pressure of a transparent gas to the mixture.

Studies of very reactive compounds and radicals formed during reactions have been aided by development of the matrix isolation method.^{141, 142} In this technique the gaseous substance to be studied is rapidly mixed with an inert transparent medium, such as nitrogen or argon, and quickly frozen on a cold window maintained at very low temperature. The reactive material is trapped in an inert matrix and cannot react or decay. This method has been used, for example, to study the radicals produced in high frequency electrical discharges.^{143, 144}

Another subject of current interest is the study of adsorbed molecules. Gases are exposed to active surfaces in the form of fine layers of silica powder,¹⁴⁵ porous glass,¹⁴⁶ aerosil silica,¹⁴⁷ or catalyst embedded in potassium bromide pellets.¹⁴⁸ In many cases the mechanism of chemisorption can be defined by observing absorption bands associated with unsaturated bonds.^{149, 150}

Solid Samples

Solid samples occur in a large variety of forms—crystalline, amorphous, film, powder, gel, or plate. Before an infrared spectrum can be obtained it is necessary to form the sample into a shape approximating a thin layer. Often this is done by placing the solid in solution, and treating it as a liquid sample.

The occasional sample submitted in the form of an unsupported film of proper size, usually at least 0.5×2.5 cm, and about 0.02 to 0.1 mm thick, can be observed directly by mounting it in the radiation beam. Other samples can often be formed into thin films by a variety of methods. Solutions poured on mercury, smooth plastic (such as polyethylene), glass, or polished metal will leave a film, after the solvent has evaporated, which can then be stripped off. In the case of films formed on thin plastic, the spectrum can be obtained directly, with the spectrum of the plastic superposed. Films cast on metal surfaces are sometimes lifted electrolytically.¹⁶¹ Solid samples can also be formed into thin films by rolling, by pressing between metal platens or sheets of metal foil or plastic,¹⁶² sometimes with the application of heat, by slicing a thin layer with a microtome¹⁶³ or by melting the sample and allowing it to solidify on a flat surface or between surfaces. These procedures avoid the trapping of residual solvent often encountered in the evaporated film technique. The spectra of unsupported films frequently show interference fringes due to internal reflections from the smooth surfaces. These can be eliminated by roughening the surface, or by coating the surfaces with thin liquid films,¹⁶⁴ at the expense sometimes of reduced energy or unwanted absorption bands. The thickness of unsupported films can be determined with a micrometer or other mechanical thickness gauge, by β -ray absorption,¹⁶⁵ or by using the material as a spacer in a Fabry-Perot interferometer.¹⁶⁶ Film thickness can often be controlled in the evaporated solvent technique by spreading viscous solutions of fixed concentration between spacer strips before evaporation¹⁶⁷ or by spreading the solutions with a notched tool (doctor blade) to give reproducible thicknesses.

Films can also be cast by solvent evaporation or from a melt on or between suitable windows.¹⁶⁸ This technique is particularly suited to crystalline substances which are

deposited on the window in polycrystalline films¹⁶⁹ or to biological substances, such as bacterial films.^{160, 161, 162} Films can be formed between windows by pressure in some cases. Plastic materials can be squeezed between windows of mica, polyethylene, or silver chloride¹⁶³ or even sodium chloride¹⁶⁴ if care is taken to avoid cracking the windows. Somewhat harder materials can also be formed by pressure between salt windows¹⁶⁵ if the sample area is small relative to the window size. This requires the use of a beam condensing device.

Polycrystalline films can be deposited on cold surfaces by vacuum sublimation.^{121, 166, 167, 168, 169, 170, 171} Thin metal films have been studied in this way by deposition on thin (300Å) layers of aluminum oxide.¹⁷² An analogous technique, which is also applicable to normally liquid or gaseous samples, makes use of a low temperature cell to solidify the sample.^{173, 174, 175, 176} Such cells can be used to study the transformations which many compounds undergo at reduced temperature.¹⁷⁷ These cells take a variety of forms, varying from simple cells cooled only slightly below room temperature, through very elaborate evacuated chambers with samples mounted on cold fingers cooled to liquid nitrogen or even liquid helium temperatures.¹⁷⁸ Samples are sometimes condensed on a cold, highly polished metal surface which reflects the radiation, causing it to pass through the sample twice.^{166, 167, 179} In other cell designs, the sample is condensed between cooled windows. If conditions are ideal thin single crystals can be grown by vacuum sublimation,^{180, 181, 182} but usually when it is desired to study single crystals they are obtained in a less convenient form and must be cleaved or ground to the proper thickness. Grinding is difficult because of the thin sections required, but it is sometimes possible to glue a crystal on a glass plate, grind it, and then float it free in a dish of solvent where it can be transferred to a mounting ring.²⁵ Alternatively, if the crystal

is attached to a salt plate for grinding it need not be removed, provided the absorption of the adhesive can be tolerated.

Powdered samples are perhaps most often encountered in infrared spectroscopy of solids and a number of techniques for handling them have been devised. The most direct approach is to spread a layer of powder on a window and obtain a spectrum by direct transmission, but the energy losses from scatter are^{183, 184, 185} frequently prohibitive unless the particles are very small. In some applications the powder is suspended in a volatile solvent which is permitted to evaporate leaving a layer of particles on the window.¹⁸⁶ Powder can be ground into a fine consistency with the usual laboratory devices (mortar and pestle, etc.), but a number of special techniques have been devised, such as use of a diamond-surfaced spatula.¹⁸⁷ Fine particles can be isolated by means of sedimentation in liquid,¹⁸⁸ in an air stream,¹⁸⁹ by electrostatic means,¹⁹⁰ or with graded sieves.

Scatter losses can be reduced by suspending the particles in a liquid medium of approximately the same refractive index. Usually the medium selected is mineral oil or "Nujol" and the technique has become known as the Nujol mull technique. However, other liquids or even solids¹⁹¹ are useful provided they are sufficiently transparent in the desired region and have the proper refractive index.^{165, 192} Some materials have a rather large change in refractive index in the vicinity of absorption bands. As the refractive index of the particles becomes equal to that of the surrounding medium the scatter vanishes and the spectrum shows a narrow region of unusually high transmission. This phenomenon is called the Christiansen Filter Effect.^{193, 194} It can be minimized by grinding the powder to a very fine particle size with appropriate grinders.¹⁹⁵ Some workers prefer to grind the powder between unpolished salt windows which have previously been ground with fine emery paper.^{196, 197}

Rubbery materials can be prepared by grinding with an abrasive such as sodium chloride¹⁹⁸ or by grinding at very low temperature. The dispersion of particles in liquid can sometimes be assisted with a material like aluminum stearate¹⁹⁹ or by exposure to supersonic radiation.²⁰⁰ It is helpful to use a window with an annular groove^{201, 205} in the demountable cell used for mulls. This prevents excess material from being trapped under the spacer and permits better reproducibility of cell thickness. However, quantitative analysis of powder samples, when it is possible at all, is usually accomplished with the aid of an internal standard as a means of determining cell thickness.^{202, 203, 204} In quantitative analysis it is particularly important to control the particle size because, in addition to the dependence of scattered radiation, the apparent absorptivity also depends on particle size.^{161, 205-209}

A refinement of the mull technique, known as the KBr-pellet technique, was developed independently by several workers.^{210, 211, 212, 213} It consists of mixing the solid sample with a quantity of an alkali-halide powder, usually potassium bromide, and pressing the mixture in a die to produce a transparent or translucent disk. The disk is mounted directly in the spectrometer. Other alkali-halides^{214, 215} can be chosen to provide a better refractive index match in controlling scatter.¹⁶⁵ A large variety of die designs have been reported in the literature, as well as methods of treating^{216, 217} and measuring materials.^{218, 219} Sample and alkali halide can be mixed by grinding together in a mortar, ball mill or other mechanical device, by mixing a slurry of alkali halide in a solution containing the sample and allowing the solvent to evaporate, or by freeze drying a solution of the sample—alkali halide mixture in water or an organic solvent. Methods of preparing microgram quantities of sample in small pellets^{73, 220, 221} have been devised for use with beam condensing devices.⁷² Pressed pellets have been found to be me-

chanically stable, permitting the observation of spectra at elevated²²² and reduced temperatures and even permitting the study of thermal decomposition of samples mounted in pellets.²²³ It is possible to perform quantitative analyses with pelleted samples,²²⁴⁻²²⁹ with or without the use of internal standards, but it is essential to control the particle size very closely or reduce it to a very small value, just as in the case of mulls. There are certain difficulties^{214, 215, 230-249} associated with the use of the pellet technique, and caution is required in its application. Some materials will react with alkali halides under pressure or during grinding either immediately or over a longer period of time. Other substances are transformed into different crystal habits, which can result in very different spectra. Comparison with spectra of Nujol mulls will usually show whether these changes have occurred but one must be certain that spectral differences are not due to solution of the sample in the mineral oil or to crystallite orientation caused, for example, by sliding the windows together.²⁵⁰ In addition, it is possible to contaminate the alkali halide during grinding by abrasion of the mortar material.^{251, 252}

Because molecules in crystalline lattices are arranged in fixed positions and orientations the directions of their molecular vibrations are also fixed. It is known that an oscillating dipole can absorb radiation only when the direction of vibration coincides with the direction of the electric vector of the radiation. Hence if the beam from a spectrometer source is polarized it is possible to determine the direction of a given vibration by rotating the crystal until maximum absorption is obtained.^{253, 254, 255, 256, 257, 258} A number of devices for producing polarized radiation have been constructed, mostly based on the principle that light reflected at the proper angle (Brewster's angle) from a dielectric is totally polarized. Usually, the radiation transmitted by several layers of selenium or silver chloride is used instead

of reflected light. Because the radiation passed by spectrometers is also somewhat polarized by reflection from prism faces and gratings,²⁵⁹ it is common practice to adjust the polarizer for maximum energy and rotate the sample. It is not easy to obtain single crystals of sufficient size for infrared study. Hence in making measurements on oriented crystals with polarized radiation, spectroscopists often attempt to grow polycrystalline layers with the individual crystal axes lying in largely the same direction.²⁶⁰ This can sometimes be done by crystallization in a thermal gradient or by starting the precipitation at one point by application of a cold spot or a seed crystal. Sometimes the growth of crystallites will be influenced by the crystal structure of the windows containing the melt and often unusual window materials such as mica are used²⁶¹ to take advantage of this. Some window materials will be more effective orienting agents if rubbed in one direction before use.²⁶² Amorphous and plastic materials can often be oriented by stretching or rolling,^{263, 264, 265} and studied with the stretch-axis parallel and normal to the direction of polarization. Solid films are frequently oriented relative to their surface, but otherwise randomly arranged. In this case, use of polarized radiation will not reveal the orientation, but a comparison of a spectrum of the film with a spectrum of the same material prepared by one of the powder methods can show which of the molecular vibrations are predominantly perpendicular to the film surface and which are predominantly parallel.²⁶⁶⁻²⁷¹ The perpendicular modes will be weaker in films than in powder samples, while the converse will be true for the parallel modes. Similar information can sometimes be obtained by tilting the film in the beam.²⁶⁵

Fibers are special cases of oriented samples. They can be studied with polarized or natural light by carefully aligning them in a common direction.²⁷²⁻²⁷⁷ They can be mounted dry if scatter is not too severe, or

they can be coated with a liquid medium. Fibers can also be carefully aligned between layers of alkali halide powder and pressed into pellets. For studies of unoriented fibers, they can be chopped into short lengths with a sharp instrument or in a mill and pressed into pellets.

A property associated with the spectra of crystalline solids is the frequent occurrence of fine structure or line splitting due to the interactions of neighboring molecules in a unit lattice cell or to the combination of molecular and lattice modes of vibration. These effects are interesting in themselves, but it is often desirable to eliminate them while retaining the characteristic sharpness of solid phase spectra. This can sometimes be done by diluting the molecules of interest in a mixed crystal, for example, naphthalene in anthracene,²⁷⁸ or in a solid solution, such as complex ions in alkali-halide lattices.^{279, 280} A related technique is concerned with the formation of mixed crystals of isotopic molecules.^{281, 282}

Infrared spectroscopy is useful in the study of reactions and reaction products. Cells have been constructed for the controlled exposure of solid films to gases^{283, 284, 285} in such a way that spectra can be recorded during the ensuing reaction.

Infrared studies on solids are not limited to absorption spectroscopy. Specular reflection spectra have also been useful to some extent,^{286, 287} for example in the identification of gems.²⁸⁸ Diffuse reflectance can be measured by means of integrating spheres,^{289, 290} but this technique has been less useful in the infrared than in the visible regions of the spectrum. Reflection bands of organic compounds are generally quite weak, but frequently reflectance techniques are used to obtain absorption spectra of thin films deposited on reflecting surfaces. This approach has been extended to exceedingly thin layers by use of multiple reflections.²⁹¹ Emission spectra of solids have also been studied, either directly by observing radiation

emitted from a hot sample²⁹² or indirectly by correlating the reflectance of a hot, opaque sample with its emissivity.²⁹³ It is sometimes possible to study coatings on filaments by observing the emission properties of the sample. The refractive index of solids in the infrared region is another potentially useful property. It can be determined by constructing a solid prism²⁹⁴ and measuring the deviation of radiation, by observing interference fringes produced by a thin film of known thickness, or by measuring the reflectivity which is related to the refractive index.

Purification and Treatment of Complex Samples

It is frequently desirable and sometimes essential to pre-treat samples submitted for infrared analysis in order to remove impurities or to transform the material into a more readily handled form. The pyrolysis technique¹⁰⁸⁻¹⁰⁷ mentioned above is an example of the latter. Other types of reaction have also been used.²⁹⁵ For example, the salts of acids often have more characteristic spectra than the acids themselves.²⁹⁶

Purification of samples can range from a rough treatment to remove water, such as the use of 2,2-dimethoxypropane as a drying agent,²⁹⁷ to very highly refined fractionation methods like those used by the American Petroleum Institute in preparing pure hydrocarbon samples for infrared reference spectra.

The current popularity of gas chromatography has led to the combined use of this powerful quantitative tool with infrared spectroscopy for qualitative identification of fractions^{69, 298-305} and quantitative analysis for components not easily separated by the chromatograph.^{306, 307} Because of the small sample size often encountered in gas chromatography micro- or semi-micro infrared techniques are usually required. However, recent developments in preparative scale gas chromatography have provided a useful

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method for purification of routine infrared samples in macro-quantities.³⁰⁸

Older forms of chromatography, such as liquid elution^{309, 310, 311, 312} and paper chromatography,³¹³ have also been used in the preparation of samples, the latter requiring micro-techniques. Other methods include fractional crystallization of solids^{314, 315} and low temperature distillation of gases.^{316, 317}

BIBLIOGRAPHY

General references on preparation of samples and cells

WILLIAMS, V. Z., "Infrared Instrumentation and Techniques," *Rev. Sci. Inst.*, **19**, 135 (1948).

BARNES, R. B., GORE, R. C., LIDDEL, U., AND WILLIAMS, V. Z., "Infrared Spectroscopy, Industrial Applications and Bibliography," Reinhold Publishing Co., New York, 1944.

RANDALL, H. M., FOWLER, R. G., FUSON, N., AND DANGL, J. R., "Infrared Determination of Organic Structures," D. Van Nostrand Co., New York, 1949.

BRUGEL, W., "Einführung in die Ultrarotspektroskopie," Stein Kopff, Darmstadt, 1954 (Revised 1958).

CLARK, C., "Infrared Spectrophotometry" Physical Techniques in Biological Research, Oster and Pollister, Ed., Vol. I, Academic Press, Inc., New York, 205-323, 1955.

HOYER, H., "Infrarotspektroskopie" in Houben-Weyl Methoden der Organischen Chemie, E. Muller, ed., Band III, Teil 2, Physikalische Forschungsmethoden, Georg Thieme Verlag, Stuttgart, 795-900, 1955.

JONES, R. N. AND SANDORFY, C., "The Application of Infrared and Raman Spectroscopy to the Elucidation of Molecular Structure," Physical Methods of Organic Chemistry, Chemical Applications of Spectroscopy, Weissberger, ed., Vol. IX, Interscience, New York, 246-560, 1956.

SMITH, R. A., JONES, F. E., AND CHASMAR, R. P., "The Detection and Measurement of Infrared Radiation," Oxford University Press, London, 1957.

LECOMTE, J., "Spectroscopie dans l'infrarouge," Handbuch der Physik XXVI, pp. 244-937, Springer-Verlag, Berlin, 1958.

Cell construction and materials

1. LORD, R. C., McDONALD, R. S., AND MILLER, F. A., "Notes on the Practice of Infrared

Spectroscopy," *J. Opt. Soc. Am.*, **42**, 149 (1952).

2. MCGOVERN, J. J. AND FRIEDEL, R. A., "Infrared Filters and Cells of Unpolished Salt Crystals," *J. Opt. Soc. Am.*, **37**, 660 (1947).

3. SLOWINSKI, E. J., JR., "Note on the Polishing of Rock-Salt Windows," *J. Opt. Soc. Am.*, **44**, 342 (L) (1954).

4. ANDERSON, SCOTT, ANDERSON, W. J., AND KRAKOWSKI, M., "Water-Proofing Rock-Salt for Infrared Absorption Cells," *Rev. Sci. Inst.*, **21**, 574 (1950).

5. SLOWINSKI, E. J., JR., "Note on the Polishing of Fluorite Windows," *J. Opt. Soc. Am.*, **47**, 1034 (L) (1957).

6. YODER, P. R., JR. AND BOERNER, R., "Polishing Agent for KRS-5 Crystals," *J. Opt. Soc. Am.*, **43**, 808 (1953).

7. FUOSS, R. M., "Silver Chloride Windows for Infrared Cells," *Rev. Sci. Inst.*, **16**, 154 (1945).

8. FUGASSI, P. AND MCKINNEY, D. S., "The Preparation of Silver Chloride Films," *Rev. Sci. Inst.*, **13**, 335 (1942).

9. KREMEERS, H. C., "Optical Silver Chloride," *J. Opt. Soc. Am.*, **37**, 337 (1947).

10. HYMAN, MARK, JR. AND BILLINGS, BRUCE H., "High Transmission Windows for Radiation of 3 to 14 Microns Wavelength," *J. Opt. Soc. Am.*, **37**, 113 (1947).

11. MITZNER, B. M., "Technique for Polishing Silver Chloride Windows," *J. Opt. Soc. Am.*, **47**, 328 (1957).

12. SCHWEMER, W. C., MURPHY, J. E., AND WILLIAMSON, L., "Salvaging of Silver Chloride Windows," *Anal. Chem.*, **29**, 1113 (1957).

13. RYASON, RAYMOND, "On the Fabrication of Alkali Halide Windows," *J. Opt. Soc. Am.*, **43**, 928 (L) (1953).

14. WEIR, C. E., LIPPINCOTT, E. R., VALKENBURG, A. VAN, BUNTING, E. N., "Infrared Studies in the 1 to 15 micron Region to 30,000 Atmospheres," *J. Research NBS*, **63A**, 55 (1959).

15. KIRBY-SMITH, J. S. AND JONES, E. A., "Use of Polytrifluoroethoxyethylene in Infrared and Raman Spectroscopy," *J. Opt. Soc. Am.*, **39**, 780 (1949).

16. WARSCHAUER, D. M. AND PAUL, W., "Infrared Windows for Helium Cryostats," *Rev. Sci. Inst.*, **27**, 419 (1956).

17. MILLS, I. M., SCHERER, J. R., CRAWFORD, B., JR., AND YOUNGQUIST, M., "Calibration and Use of a Cesium Iodide Prism in the Infrared," *J. Opt. Soc. Am.*, **45**, 785 (1955).

18. FOLEY, H. M. AND RANDALL, H. M., "Fine

- Structure in the Far Infrared Spectrum of NH_3 ," *Phys. Rev.*, **59**, 171 (1941).
19. KIVENSON, G., ROTH, A., AND RIDER, M., "Some New Techniques in the Construction of Spectrographic Absorption Cells," *J. Opt. Soc. Am.*, **39**, 484 (1949).
 20. PALMER, F., "A Method of Attaching a Fluorite Window to Glass Apparatus," *Phys. Rev.*, **45**, 557 (1934).
 21. SIMARD, G. L. AND STEGER, J. E., "A High Temperature Sodium Chloride to Glass Vacuum Seal for Infrared Cells," *Rev. Sci. Inst.*, **17**, 156 (1946).
 22. COHN, H., INGOLD, C. K., AND POOLE, H. G., "Infrared Spectrum of Nitric and Deuteriomitric Acid Vapor. Completion of Identification of the Fundamental Frequencies. Entropy of Nitric Acid. Barrier Resisting Rotation of the Hydroxyl Group," *J. Chem. Soc.*, **4272** (1952).
 23. NIGHTINGALE, R. E., DOWNIE, A. R., ROTENBERG, D. L., CRAWFORD, B., AND OGG, R. A., "The Preparation and Infrared Spectra of the Oxides of Nitrogen," *J. Phys. Chem.*, **58**, 1047 (1954).
- Liquid samples (see also refs. 14, 123, 124)*
24. ROBINSON, D. Z., "Quantitative Analysis with Infrared Spectrophotometers," *Anal. Chem.*, **23**, 273 (1951).
 25. FRIEDEL, R. A. AND PELIPETZ, M. G., "Infrared Spectra of Coal and Carbohydrate Chars," *J. Opt. Soc. Am.*, **43**, 1051 (1953).
 26. GILDART, L. AND WRIGHT, N., "An Infrared Absorption Cell for Volatile Liquids," *Rev. Sci. Inst.*, **12**, 204 (1941).
 27. COGGESHALL, N. D., "Infrared Absorption Cell for Liquids," *Rev. Sci. Inst.*, **17**, 343 (L) (1946).
 28. COLTHUP, N., "Infrared Absorption Cell for Quantitative Analysis," *Rev. Sci. Inst.*, **18**, 64 (1947).
 29. MITZNER, B. M., "A Simple Technique for Recovering Infrared Samples," *J. Opt. Soc. Am.*, **43**, 806 (1953).
 30. RANDALL, H. M., "An Absorption Cell, Mercury Sealed," *Rev. Sci. Inst.*, **10**, 195 (1939).
 31. OETJEN, R. A., WARD, W. M., AND ROBINSON, J. A., "Simple Cell for Spectroscopic Examination of Volatile Liquids," *J. Opt. Soc. Am.*, **36**, 615 (1946).
 32. CRIDLE, E. E., GREIG, A. A., AND HUBLEY, C. E., "Contact Cell for Toxic Liquids," *Appl. Spec.*, **11**, 137 (1957).
 33. SMITH, D. C. AND MILLER, E. C., "Infrared Absorption Cells and Measurement of Cell Thickness," *J. Opt. Soc. Am.*, **34**, 130 (1944).
 34. SUTHERLAND, G. B. B. M. AND WILLIS, H. A., "Measurement of Cell Thickness," *Trans. Faraday Soc.*, **41**, 181 (1945).
 35. ELLIS, J. W., "Some Infrared Interference Spectra," *J. Opt. Soc. Am.*, **23**, 88 (1933).
 36. JAFFE, J. H. AND JAFFE, H., "Measurement of Thickness of Infrared Absorption Cells," *J. Opt. Soc. Am.*, **40**, 53 (1950).
 37. FOX, J. J. AND MARTIN, A. E., "Investigations of Infrared Spectra (2.5-7.5 μ) Absorption of Water," *Proc. Roy. Soc. (London)*, **A174**, 234 (1940).
 38. NIELSON, J. R. AND SMITH, D. C., "Analysis by Infrared Spectroscopy. A New Method Applied to Mixtures of Nitroparaffins," *Ind. Eng. Chem., Anal. Ed.*, **15**, 609 (1943).
 39. BENNING, A. F., EBERT, A. A., AND IRWIN, C. F., "Determination of Small Amounts of Water in Gases and Liquids by Infrared Spectrometry," *Ind. Eng. Chem., Anal. Ed.*, **19**, 867 (1947). Also *Refrig. Eng.*, **55**, 166 (1948).
 40. DIAMOND, W. J., "Water Determination in Oil-Contaminated "Freon-12" by Infrared Spectrophotometry," *Appl. Spect.*, **12**, 10 (1958).
 41. DIAMOND, W. J., "Water Determination in "Freon-22" Refrigerant by Infrared Spectrophotometry," *Appl. Spect.*, **13**, 77 (1959).
 42. JOHANNESSEN, R. B., GORDON, C. L., STEWART, J. E., AND GILCHRIST, R., "Application of Infrared Spectroscopy to the Determination of Impurities in Titanium Tetrachloride," *J. Res. NBS*, **53**, 197 (1954).
 43. PROSS, A. W., "Estimation of Impurities in Liquid Chlorine by Infrared Absorption Spectrophotometry," *Canadian J. Chem.*, **32**, 956 (1954).
 44. SIMARD, R. G., HASEGAWA, I., BANDARUK, W., AND HEADINGTON, C. E., "Infrared Spectrophotometric Determination of Oil and Phenols in Water," *Anal. Chem.*, **23**, 1384 (1951).
 45. TARPLEY, W. AND VITIELLO, C., "Infrared Spectra of Steroids. New Solvents for Steroids Difficultly Soluble in Carbon Disulfide," *Anal. Chem.*, **24**, 315 (1952).
 46. ARD, J. S. AND FONTAINE, T. D., "Infrared Transmitting Solvents. Triethylamine Addition as a Means of Increasing Applicability," *Anal. Chem.*, **23**, 133 (1951).
 47. PLYLER, E. K. AND ACQUISTA, N., "Infrared

- Absorption of Liquid Water from 2 to 42μ ," *J. Opt. Soc. Am.*, **44**, 505 (L) (1954).
48. GORE, R. C., BARNES, R. B., AND PETERSEN, E., "Infrared Absorption of Aqueous Solutions of Organic Acids and Their Salts," *Anal. Chem.*, **21**, 382 (1949).
49. STERNGLANZ, H., "Using Water As an Infrared Solvent," *Appl. Spect.*, **10**, 77 (1956).
50. DUVAL, C., "First Applications of Absorption Spectra in the Infrared Realized from a Drop of Aqueous Solution," *Mikrochim. Acta*, 741 (1956).
51. FALK, MICHAEL AND GIGUERE, P. A., "Infrared Spectrum of the H_2O+ Ion in Aqueous Solutions," *Canadian J. Chem.*, **35**, 1195 (1957).
52. POTTS, W. J. AND WRIGHT, N., "Quantitative Infrared Absorption Spectroscopy in Water Solution," *Anal. Chem.*, **28**, 1255 (1956).
53. ROBINSON, D. Z., "Quantitative Analysis with Infrared Spectrophotometers. Differential Analysis," *Anal. Chem.*, **24**, 619 (1952).
54. BARR, E. S., "An Adjustable Infrared Absorption Cell for Liquids," *Rev. Sci. Inst.*, **12**, 396 (1941).
55. GORDON, R. R. AND POWELL, H., "Variable Path Length Cell for the Measurement of the Absorption of Liquids in the Infrared Region of the Spectrum," *J. Sci. Inst.*, **22**, 12 (1945).
56. MITZNER, B. M. AND LEWIN, S. Z., "A Simple Variable Thickness Infrared Absorption Cell," *J. Opt. Soc. Am.*, **44**, 425 (L) (1954).
57. ADAMS, R. M. AND KATZ, J. J., "New Variable-Thickness Infrared Cell and the Infrared Spectra of HF , DF , H_2O , and D_2O ," *J. Opt. Soc. Am.*, **46**, 895 (1956).
58. MITZNER, B. M. AND LEWIN, S. Z., "Double Cell for Spectral Study of Interactions Between Substances," *J. Opt. Soc. Am.*, **44**, 499 (L) (1954).
59. STUART, A. V. AND SUTHERLAND, G. B. B. M., "Effect of Hydrogen Bonding on the Deformation Frequencies of the Hydroxyl Group in Alcohols," *J. Chem. Phys.*, **24**, 559 (1956).
60. WOLLMAN, S. H., "An Absorption Cell and Loader for Use in Microanalysis by Infrared Spectroscopy," *Rev. Sci. Inst.*, **20**, 220 (1949).
61. DAVISON, W. H. T., "New Infrared Microcell," *J. Opt. Soc. Am.*, **45**, 227 (1955).
62. BURCH, C. R., "Reflecting Microscopes," *Proc. Phys. Soc. (London)*, **59**, 41 (1947).
63. BARBER, R., COLE, A. R. H., AND THOMPSON, H. W., "Infrared Spectroscopy with the Reflecting Microscope in Physics, Chemistry, and Biology," *Nature*, **163**, 198 (1949).
64. BLOUT, E. R., BIRD, G. R., AND GREY, D. S., "Infrared Microspectroscopy," *J. Opt. Soc. Am.*, **40**, 304 (1950).
65. COLE, A. R. H. AND JONES, R. N., "A Reflecting Microscope for Infrared Spectrometry," *J. Opt. Soc. Am.*, **42**, 348 (1952).
66. COATES, V. J., OFFNER, A., AND SIEGLER, E. H., "Design and Performance of an Infrared Microscope Attachment," *J. Opt. Soc. Am.*, **43**, 984 (1953).
67. BLOUT, E. R., "Microspectroscopy," *Technique of Organic Chemistry*, Vol. 1, Chapt. XXXIII. A. Weissberger Ed., Interscience, New York, 1954.
68. BLOUT, E. R., PARRISH, M., BIRD, G. R., AND ABBATH, M. J., "Infrared Microspectroscopy III. A Capillary Cell for Liquids," *J. Opt. Soc. Am.*, **42**, 966 (1952).
69. MOLNAR, W. S. AND YARBOROUGH, V. A., "Polyethylene Capillary Tubes as Micro Liquid Cells for Infrared Spectroscopy," *Appl. Spect.*, **12**, 143 (1958).
70. JONES, R. N. AND NADEAU, A., "Cavity Type Micro-cells for Infrared Spectrometry," *Spectrochim. Acta*, **12**, 183 (1958).
71. BLACK, E. D., MARGERUM, J. D., AND WYMAN, G. M., "Sample Handling for Qualitative Infrared Microspectroscopy," *Anal. Chem.*, **29**, 169 (1957).
72. ANDERSON, D. H. AND MILLER, O. E., "Silver Chloride Beam Condensing Lens System for Micro-Infrared Measurements," *J. Opt. Soc. Am.*, **43**, 777 (1953).
73. ANDERSON, D. H. AND WOODALL, N. B., "Infrared Identification of Materials in the Fractional Milligram Range," *Anal. Chem.*, **25**, 1906 (1953).
74. WHITE, J. U., WEINER, S., ALPERT, N. L., AND WARD, W. M., "Microsampling for Small Infrared Spectrophotometers," *Anal. Chem.*, **30**, 1694 (1958).
75. MITZNER, B. M., "A Simple Method of Obtaining the Infrared Spectra of Solid Organic Samples," *J. Opt. Soc. Am.*, **43**, 806 (1953).
76. RICHARDS, R. E. AND THOMPSON, H. W., "An Absorption Cell for Molten Solids and Heated Liquids," *Trans Faraday Soc.*, **41**, 183 (1945).
77. ZENCHEL'SKY, S. T., AND SHOWELL, J. S., "Thermostated Microcell Adapter for Perkin-Elmer Infrared Spectrophotometers," *Anal. Chem.*, **29**, 167 (L) (1957).
78. MATTHEW, H. C., "A Heated Infrared Cell," *Appl. Spect.*, **9**, 177 (1955).

79. MIZUSHIMA, SAN-ICHIRO, "Structures of Molecules and Internal Rotation," Academic Press, New York, 1954.
80. COLE, A. R. H. AND MACRITCHIE, F., "The Energy of a Hydrogen Bond by Infrared Spectroscopy," *Spect. Acta*, 1959, 6.
81. LINNIG, F. J. AND STEWART, J. E., "A Constant Thickness Heated Cell for Quantitative Infrared Spectrophotometry," *Anal. Chem.* **32**, 891 (1960).
82. KAPFF, S. F., "Infrared Emission Spectra of Hot Liquids," *J. Chem. Phys.*, **16**, 446 (1948). Also *Science*, **104**, 274-5 (1946).
83. SLOWINSKI, E. J., JR. AND CLAVER, G. C., "On the Temperature Dependence of the Intensity of Infrared Absorption Bands of Liquids," *J. Opt. Soc. Am.*, **45**, 396 (1955).
84. HUGHES, R. H., MARTIN, R. J., AND COGESHALL, N. D., "Temperature Dependence of Infrared Absorption," *J. Chem. Phys.*, **24**, 489 (1956).
85. SMITH, F. A. AND CREITZ, E. C., "Pressure-Tight Infrared Absorption Cell for Liquids," *Anal. Chem.*, **21**, 1474 (1949).
86. CREITZ, E. C. AND SMITH, F. A., "Infrared Absorption Spectra of the Liquid Butenes and 1,3-Butadiene," *J. Research NBS*, **43**, 365 (1949).
87. PARSONS, R. W. AND DRICKAMER, H. G., "Sodium Chloride and Calcium Fluoride Windows for High-Pressure Infrared Spectroscopy," *J. Opt. Soc. Am.*, **46**, 464 (1956).
88. FITCH, R. A., SLYKHOUSE, T. E., AND DRICKAMER, H. G., "Apparatus for Optical Studies to Very High Pressures," *J. Opt. Soc. Am.*, **47**, 1015 (1957).
89. FISHMAN, E. AND DRICKAMER, H. G., "Equipment for High Pressure Optical and Spectroscopic Studies," *Anal. Chem.*, **28**, 804 (1956).
90. BENSON, A. M., JR. AND DRICKAMER, H. G., "Stretching Vibrations in Condensed Systems: Especially Bonds Containing Hydrogen," *J. Chem. Phys.*, **27**, 1164 (1957).
91. FISHMAN, E. AND DRICKAMER, H. G., "Effect of Pressure on the Frequency of the OH Band in Butanol Solutions," *J. Chem. Phys.*, **24**, 548 (1956).
92. BENSON, A. M. AND DRICKAMER, H. G., "The Effect of Pressure on the Vibrational Frequency of Bonds Containing Hydrogen," *Disc. Faraday Soc.*, No. 22, 39-43 (1956).
93. BIRD, G. R. AND BLOUT, E. R., "Infrared Flow Dichroism," *J. Chem. Phys.*, **25**, 798 (1956).
94. BIRD, G. R., PARRISH, M., JR., AND BLOUT, E. R., "Apparatus for the Observation of Infrared Streaming Dichroism of Polymer Solutions," *Rev. Sci. Instr.*, **29**, 305 (1958).
95. CHARNEY, E. AND HALFORD, R. S., "Dispersion of the Electro-Optic Kerr Effect in the Infrared Region," *J. Chem. Phys.*, **29**, 221 (1958).
96. HEDIGER, H. J. AND GUNTARD, Hs. H., "Optical Rotatory Power of Organic Substances in the Infrared," *Helv. Chim. Acta*, **37**, 1125 (1954).
97. KAGARISE, R. E. AND MAYFIELD, J. W., "Simple Interferometer for Dispersion Measurements of Liquids in the 2-22 μ Region," *J. Opt. Soc. Am.*, **48**, 430 (1958).
98. VINCENT-GEISSE, J. AND LECOMTE, J., "Measurement of the Dispersion of Liquids in the Infrared by an Interferometric Method," *Compt. Rend.*, **244**, 577 (1957).
99. JAFFE, J. H. AND OPPENHEIM, U., "Infrared Dispersion of Liquids by Critical Angle Refractometry," *J. Opt. Soc. Am.*, **47**, 782 (1957).
100. PFUND, A. H., "The Dispersion of CS₂ and CCl₄ in the Infrared," *J. Opt. Soc. Am.*, **25**, 351 (1935).
101. PITTMAN, M. A., "Infrared Dispersion of CHCl₃ and CHBr₃," *J. Opt. Soc. Am.*, **29**, 358 (1939).
102. JAFFE, J. H., "The Measurement of Refractive Indexes of Liquids in the Infrared," *J. Opt. Soc. Am.*, **41**, 166 (1951).
103. KRUSE, P. F., JR. AND WALLACE, W. B., "Identification of Polymers by Infrared Analysis of their Pyrolysis Products," *Anal. Chem.*, **24**, 2015 (1952).
104. KRUSE, P. F., JR. AND WALLACE, W. B., "Identification of Polymeric Materials," *Anal. Chem.*, **25**, 1156 (1953).
105. HARMS, D. L., "Identification of Complex Organic Materials," *Anal. Chem.*, **25**, 1140 (1953).
106. BENTLEY, F. F. AND RAPPAPOORT, G., "Semi-quantitative Analysis of Buna N Phenolic Blends by the Infrared Spectra of Their Pyrolyzates," *Anal. Chem.*, **26**, 1980 (1954).
107. TRYON, M., HOROWITZ, E., AND MANDEL, J., "Determination of Natural Rubber in GR-S—Natural Rubber Vulcanizates by Infrared Spectroscopy," *J. Res. NBS*, **55**, 219 (1955).

Gaseous samples (see also refs. 17, 18, 43, 85).

108. RUSSELL, D. S., "An Infrared Cell for Small Gas Samples," *Canadian J. Chem.*, **36**, 1745 (1958).
109. MITZNER, B. M. AND LEWIN, S. Z., "De-

- mountable Infrared Gas-Absorption Cell," *Anal. Chem.*, **26**, 1254 (1954).
110. HOCHHEIMER, B. F. AND MOORE, G. E., "A Simple Short-Path Absorption Cell," *J. Opt. Soc. Am.*, **45**, 891 (L) (1955).
111. STRONG, J., "Apparatus for Spectroscopic Studies in the Intermediate Infrared Region—20 to 40 μ ," *Rev. Sci. Instr.*, **3**, 810 (1932).
112. SMITH, H. D. AND MARSHALL, J. K., "Method for Obtaining Long Optical Paths," *J. Opt. Soc. Am.*, **30**, 338 (1940).
113. KRATZ, H. R. AND MACK, J. E., "An Improved Method for Obtaining a Long Optical Path in a Limited Space," *Phys. Rev.* **57**, 1059(A) (1940).
114. KRATZ, H. R. AND MACK, J. E., "A Long Optical Path in a Restricted Space," *J. Opt. Soc. Am.*, **32**, 457 (1942).
115. WHITE, J. U., "Long Optical Paths of Large Aperture," *J. Opt. Soc. Am.*, **32**, 285 (1942).
116. TAYLOR, J. H., BENEDICT, W. S., AND STRONG, J., "Infrared Spectra of H₂O and CO₂ at 500°C," *J. Chem. Phys.*, **20**, 1884 (1952).
117. STEPHENS, E. R., "Long Path Infrared Spectroscopy for Air Pollution Research," *Appl. Spect.*, **12**, 80 (1958).
118. WHITE, J. U. AND ALPERT, N. L., "Wide Range Infrared Absorption Cell," *J. Opt. Soc. Am.*, **48**, 460 (1958).
119. HOWARD, J. N., BURCH, D. E., AND WILLIAMS, D., "Infrared Transmission of Synthetic Atmospheres—I Instrumentation," *J. Opt. Soc. Am.*, **46**, 186 (1956).
120. WHITE, J. U., ALPERT, N. L., WARD, W. M., AND GALLAWAY, W. S., "Microgas Cell for Infrared Spectroscopy," *Anal. Chem.*, **31**, 1267 (1959).
121. STEWART, J. E., "Low-Temperature Microcell for Infrared Study of Condensed Gases," *Anal. Chem.*, **30**, 2073 (1958).
122. COULON, R., "Accessory to Perkin-Elmer Infrared Spectrometer for Using Long Cells with Small Openings," *J. Phys. Radium*, **16**, 343 (1955).
123. PAILLARD, G., "A Contribution to the Study of Dissolved Gases by Infrared Spectroscopy," *J. Phys. Radium*, **16**, 281 (1955).
124. LUTHER, H. AND HIEMENZ, W., "Solubility and Infrared Spectra of Gases in Liquids. Part I. Description of Apparatus and Method of Solubility Measurements," *Chem.-Ing.-Tech.*, **29**, 530 (1957).
125. BERNSTEIN, H. J., "Internal Rotation V The Energy Difference Between the Rotational Isomers of 1, 2—Dibromoethane," *J. Chem. Phys.*, **18**, 897 (1950).
126. NEU, J. T., "Construction of a Dual Beam Heated Infrared Cell," *J. Opt. Soc. Am.*, **43**, 520 (1953).
127. SMITH, L. G., "An Infrared Absorption Cell for Gases at High and Low Temperature," *Rev. Sci. Instr.*, **13**, 65 (1942).
128. FUNK, E., "Infrared Absorption Cells for Measurements at Various Temperatures," *Optik, Berl.*, **13**, 524 (1956).
129. NEU, J. T., "Infrared Spectrographic Studies of Pre-flame Reactions of n-Butane," *J. Phys. Chem.*, **60**, 320 (1956).
130. SIMARD, G. L., STEGER, J., MARINER, T., SALLEY, D. J. AND WILLIAMS, V. Z., "In Situ Study of the Thermal Decomposition of Ethylene Oxide by Infrared Spectrometry," *J. Chem. Phys.*, **16**, 836 (1948).
131. DOWS, D. A. AND PORTER, R. F., "Infrared Emission of B₂O₃(g)," *J. Am. Chem. Soc.*, **78**, 5165 (1956).
132. DONOVAN, R. E. AND AGNEW, W. G., "Infrared Spectrum of Two-Stage Cool Flame of Diethyl Ether," *J. Chem. Phys.*, **23**, 1592 (1955).
133. DONOVAN, R. E., "Infrared Spectrum of the Two-Stage Cool Flame of Acetaldehyde," *J. Chem. Phys.*, **27**, 324 (1957).
134. DICKSON, A. D., CRAWFORD, B. L., JR. AND ROTENBERG, D. L., "Infrared Spectra of Propellant Flames," *Ind. Eng. Chem.*, **48**, 759 (1956).
135. WILKINSON, G. R., FORD, M. A. AND PRICE, W. C., "The Emission Spectra of Molecules and Radicals in the Infrared," Institute of Petroleum, London, p. 192, 1955.
136. COHEN, D., LOWE, R. AND HAMPSON, J., "Infrared Emission from High-Frequency Discharges in Carbon Dioxide," *J. Appl. Phys.*, **28**, 737 (1957).
137. PRISTERA, F. AND CASTELLI, A., "Weighing Pipette Method for Preparing Infrared Gas Standards for Ether and Alcohol," *Anal. Chem.*, **27**, 457 (1955).
138. FRIEDEL, R. A. AND QUEISER, J. A., "Quantitative Infrared Vapor Spectra," *Anal. Chem.*, **29**, 1362 (1957).
139. OLSEN, A. L. AND KRUSE, H. W., "Agitating System for Gases in Infrared Absorption Cell," *Anal. Chem.*, **29**, 1242 (1957).
140. COGGESHALL, N. D. AND SAUER, E. L., "Pressure Broadening in the Infrared and Optical Collision Diameters," *J. Chem. Phys.*, **15**, 65 (1947).
141. WHITTLE, E., DOWS, D. A. AND PIMENTEL, G. C., "Matrix Isolation Method for the Experimental Study of Unstable Species," *J. Chem. Phys.*, **22**, 1943 (L) (1954).

142. BECKER, E. D. AND PIMENTEL, G. C., "Spectroscopic Studies of Reactive Molecules by the Matrix Isolation Method," *J. Chem. Phys.*, **25**, 224 (1956).
 143. DOWS, D. A., PIMENTAL, G. C. AND WHITTLE, E., "Infrared Spectra of Intermediate Species in the Formation of Ammonium Azide from Hydrazoic Acid," *J. Chem. Phys.*, **23**, 1606 (1955).
 144. HARVEY, K. B. AND BASS, A. M., "Infrared Absorption of Oxygen Discharge Products and Ozone at 4°K," *J. Mol. Spect.*, **2**, 405 (1958).
 145. EISECHENS, R. P., PLISKIN, W. A. AND FRANCIS, S. A., "Infrared Spectra of Chemisorbed Carbon Monoxide," *J. Chem. Phys.*, **22**, 1786 (L) (1954).
 146. SIDOROW, A. N., "Study of Adsorption on Porous Glass Using Infrared Spectra," *J. Phys. Chem., Moscow*, **30**, 995 (1956).
 147. McDONALD, R. S., "Study of the Interaction Between Hydroxyl Groups of Aerosil Silica and Adsorbed Non-Polar Molecules by Infrared Spectrometry," *J. Am. Chem. Soc.*, **79**, 850 (1957).
 148. FRENCH, R. O., WADSWORTH, M. E., COOK, M. A. AND CUTLER, I. B., "The Quantitative Application of Infrared Spectroscopy to Studies in Surface Chemistry," *J. Phys. Chem.*, **58**, 805 (1954).
 149. PLISKIN, W. A. AND EISECHENS, R. P., "Infrared Spectra of Chemisorbed Olefins and Acetylene," *J. Chem. Phys.*, **24**, 482 (1956).
 150. EISECHENS, R. P., "Infrared Spectra of Chemisorbed Molecules," *J. Chem. Educ.*, **35**, 385 (1958).
- Solid Samples (see also refs. 25, 72, 73, 121)*
151. SZYMANSKI, H. A. AND CONLEY, R. T., "Electrolytic Lifting of Films from Metals for Infrared Analysis," *Anal. Chem.*, **30**, 552 (1958).
 152. LINNIG, F. J. AND STEWART, J. E., "Infrared Study of Some Structural Changes in Natural Rubber During Vulcanization," *J. Research NBS*, **60**, 9 (1958).
 153. THOMAS, L. C., AUSTIN, L. AND DAVIES, D. R., "The Examination of Nervous Tissue by Infrared Spectrophotometry," *Spectrochim. Acta*, **6**, 320 (1954).
 154. LUTINSKI, C., "Method for Elimination of Interference Fringes in Spectra of Thin Films," *Anal. Chem.*, **30**, 2071 (1958).
 155. PETERSON, J. H. AND DOWNING, J. R., "Film Thickness Measurements for Infrared Spectrophotometry," *J. Opt. Soc. Am.*, **41**, 862 (1951).
 156. HARVEY, M. R., STEWART, J. E., AND ACHHAMMER, B. G., "Index of Refraction and Particle Size as Factors in the Infrared Spectrophotometry of Polyvinylchloride," *J. Research NBS*, **56**, 225 (1956).
 157. DINSMORE, H. L. AND SMITH, D. C., "Analysis of Natural and Synthetic Rubber by Infrared Spectroscopy," *Anal. Chem.*, **20**, 11 (1948).
 158. HAUSDORFF, H. H., "Short Cuts to the Analysis of Plastics by Infrared Spectroscopy," *Soc. for Appl. Spect. Bull.*, Aug. 1951, pp. 1-5.
 159. WICKERSHEIM, K. A., "Preparation of Thin Crystalline Samples of the Alkali Hydroxides for Infrared Absorption Studies," *J. Chem. Phys.*, **29**, 1197 (L) (1958).
 160. GREENSTREET, J. E. S. AND NORRIS, K. P., "The Existence of Differences Between the Infrared Absorption Spectra of Bacteria," *Spectrochim. Acta*, **9**, 177 (1957).
 161. ROCKWOOD, S. W. AND CLARK, H. P., "Adjustable Silver Chloride Disk Holder for Infrared Spectrophotometry of Dried Bacterial Film," *Rev. Sci. Inst.*, **27**, 877 (1956).
 162. STEVENSON, H. J. R. AND BOLDUAN, O. E. A., "Infrared Spectrophotometry as a Means for Identification of Bacteria," *Science*, **116**, 111 (1952).
 163. SANDS, J. D. AND TURNER, G. S., "New Development in Solid Phase Infrared Spectroscopy," *Anal. Chem.*, **24**, 791 (1952).
 164. MITZNER, BERNARD M., "A Technique for Obtaining the Infrared Absorption Spectra of High Gel Rubbers," *J. Polymer Science*, **21**, 323 (1956).
 165. STEWART, J. E., "A Sampling Technique for Infrared Spectroscopy of Solids," *Anal. Chem.*, **31**, 1287 (1959).
 166. CONN, G. R. T., LEE, E. AND SUTHERLAND, G. B. B. M., "Investigation on the Vibration Spectra of Certain Condensed Gases at the Temperature of Liquid Nitrogen. I. Experimental Methods," *Proc. Roy. Soc. (London)*, **A176**, 484 (1940).
 167. AVERY, W. H. AND ELLIS, C. F., "Infrared Spectra of Hydrocarbons I. Some Investigations of the Temperature Dependence of Absorption Bands," *J. Chem. Phys.*, **10**, 10 (1942).
 168. REINKOBER, O., "Infrared Absorption Spectra of Solids in Thin Layers," *Z. Physik*, **5**, 192 (1921).
 169. SINSEHIMER, R. L., SCOTT, J. F. AND LOOFBOUROW, J. R., "Use of Thin Films of Sublimates for Absorption Spectroscopy," *Nature*, **164**, 796 (1949).

INFRARED SPECTROPHOTOMETRY

170. WAGNER, E. L. AND HORNIG, D. F., "The Vibrational Spectra of Molecules and Complex Ions in Crystals. III. Ammonium Chloride and Deutero-Ammonium Chloride," *J. Chem. Phys.*, **18**, 296 (1950).
171. TYLER, J. E. AND EHRLHARDT, S. A., "Infrared Spectra of Evaporated Films," *Anal. Chem.*, **25**, 390 (1953).
172. HARRIS, L., "Preparation and Infrared Properties of Aluminum Oxide Films," *J. Opt. Soc. Am.*, **45**, 27 (1955).
173. JONES, A. V., Ph.D. Dissertation, Cambridge University (1949).
174. HOLDEN, R. B., TAYLOR, W. J. AND JOHNSTON, H. L., "A Variable-Thickness Low-Temperature Infrared Cell," *J. Opt. Soc. Am.*, **40**, 757 (1950).
175. STEIN, R. S., AND SUTHERLAND, G. B. B. M., "Effect of Intermolecular Interactions Between CH Frequencies on the Infrared Spectra of N-Paraffins and Polythene," *J. Chem. Phys.*, **22**, 1993 (1954).
176. JANZ, G. J. AND FITZGERALD, W. E., "A Low Temperature Infrared Assembly," *Appl. Spect.*, **9**, 178 (1955).
177. MARKOVA, G. S., SABOVSKAJA, AND KARGIN, V. A., "Infrared Spectral Changes Due to Softening and Hardening of Crystalline and Amorphous Polymers," *J. Phys. Chem., Moscow*, **30**, 437 (1956).
178. MCMAHON, H. O., HAINER, R. M. AND KING, G. W., "A Low Temperature Infrared Transmission Cell," *J. Opt. Soc. Am.*, **39**, 786 (1949).
179. AVERY, W. H. AND MORRISON, J. R., "Infrared Spectra of Hydrocarbons. II. Analysis of Octane Mixtures by the Use of Infrared Spectra Obtained at Low Temperatures," *J. Appl. Phys.*, **18**, 960 (1947).
180. NEWMAN, R. AND BADGER, R. M., "Infrared Spectra of Cyanuric Acid and Deutero Cyanuric Acid," *J. Am. Chem. Soc.*, **74**, 3545 (1952).
181. ZWERDLING, S. AND HALFORD, R. S., "Direct Production of Spectroscopic Specimens from Single Crystals by Controlled Growth from a Vapor," *J. Chem. Phys.*, **23**, 2215 (1955).
182. ZWERDLING, S. AND HALFORD, R. S., "Motions of Molecules in Condensed Systems. IX. Infrared Absorption Anisotropy and Induced Molecular Motion in a Single Crystal of Benzene," *J. Chem. Phys.*, **23**, 2221 (1955).
183. PFUND, A. H., "The Optical Properties of Metallic and Crystalline Powders," *J. Opt. Soc. Am.*, **23**, 375 (1933).
184. LECOMTE, JEAN., "The Powder Method of Obtaining Infrared Absorption Spectra," *Cahiers Phys.*, **17**, 1 (1943).
185. LECOMTE, J., "Powder Method for Obtaining Infrared Absorption Spectra; Its Possibilities and Difficulties," *J. Phys.*, **12**, 827 (1951).
186. HUNT, J. M., WISHERD, M. P. AND BONHAM, L. C., "Infrared Absorption Spectra of Minerals and Other Inorganic Compounds," *Anal. Chem.*, **22**, 1478 (1950).
187. DEVANEY, R. G. AND THOMPSON, A. L., "An Improved Technique for Preparing Samples of Organic Solids for Infrared Analysis," *Appl. Spect.*, **12**, 154 (1958).
188. HENRY, R. L., "The Transmission of Powder Films in the Infrared," *J. Opt. Soc. Am.*, **38**, 775 (1948).
189. ROLLER, P. S., "Separation and Size Distribution of Microscopic Particles—an Air Analyzer for Fine Powders," U.S. Bureau of Mines Tech. Paper No. 490 (1931).
190. HAZEBROCK, H. F., "Electrostatic Sample Preparator for Infrared Spectroscopy of Powders," *Spect. Acta*, **1**, 1959.
191. YOSHINAGA AND OETJEN, R. A., "Sampling Techniques for Transmission Measurements in the Far Infrared," *J. Opt. Soc. Am.*, **45**, 1085 (1955).
192. ARD, JESSE S., "Mull and Solvent Media for Infrared Use," *Anal. Chem.*, **25**, 1743 (1953).
193. BARNES, R. B. AND BONNER, L. G., "The Christiansen Filter Effect in the Infrared," *Phys. Rev.*, **49**, 732 (1936).
194. PRICE, W. C. AND TETLOW, K. S., "Infrared Christiansen Filter Effect in Slurries of Organic Crystals," *J. Chem. Phys.*, **16**, 1157 (1948).
195. ARD, J. S., "Grinders for Mulling Infrared Microsamples," *Anal. Chem.*, **25**, 1780 (1953).
196. DECIUS, J. C., "Intermolecular Coupling of the Out-of-Plane Bending Mode in Several Carbonates," *J. Chem. Phys.*, **22**, 1946 (L) (1954).
197. DECIUS, J. C., "Coupling of the Out-of-Plane Bending Mode in Nitrates and Carbonates of the Aragonite Structure," *J. Chem. Phys.*, **23**, 1290 (1955).
198. RIPPERS, R. E., "Preparation of Mulls of Rubbery Materials for Infrared Examination," *Anal. Chem.*, **25**, 363 (1953).
199. DOLINSKY, M. J., "A Technique for Infrared Analysis of Solids Insoluble in Nonpolar Solvents," *J. Assoc. Offic. Agr. Chemists*, **34**, 748 (1951).
200. LARSSON, L., "Infrared Absorption Spectra

- of some Amino Acids Between 2 and 15μ ," *Acta Chem. Scand.*, **4**, 27 (1950).
201. ARD, J. E., "New Media, Techniques and Devices for Infrared Spectrometry," *Anal. Chem.*, **23**, 680 (1951).
 202. BARNES, R. B., GORE, R. C., WILLIAMS, E. F., LINSLEY, S. G. AND PETERSEN, E. M., "Infrared Analysis of Crystalline Penicillins," *Anal. Chem.*, **19**, 620 (1947).
 203. KUENTZEL, L. E., "Calcium Carbonate as an Internal Standard for Quantitative Infrared Analysis," *Anal. Chem.*, **27**, 301 (1955).
 204. BRADLEY, K. B. AND POTTS, W. J., JR., "The Internally Standardized Nujol Mull as a Method of Quantitative Infrared Spectroscopy," *Appl. Spect.*, **12**, 77 (1958).
 205. OTVOS, J. W., STONE, H. AND HARP, W. R., JR., "Theory of Radiant-Energy Absorption by Randomly Dispersed Discrete Particles," *Spectrochim. Acta*, **9**, 148 (1957).
 206. LEJEUNE, R. AND DUYCKAERTS, G., "Note Concerning the Infrared Spectra of Powders," *Spectrochim. Acta*, **6**, 194 (1954).
 207. DUYCKAERTS, G., "Contribution to Quantitative Analysis of Infrared Absorption Spectra of Powders I. Theoretical Examination of the Question," *Spectrochim. Acta*, **7**, 25 (1955).
 208. BONHOMME, J., "Contribution to Quantitative Analysis of Infrared Absorption Spectra of Powders. II. Experimental Study," *Spectrochim. Acta*, **7**, 32 (1955).
 209. STEWART, J. E., "Absorption of Radiant Energy by Solid Particles in Suspension," *J. Research NBS*, **54**, 41 (1955).
 210. COOK, E. S., KREKE, C. W., BARNES, E. B. AND MOTZEL, W., "Infrared and Ultraviolet Absorption Spectra of Proteins in the Solid State," *Nature*, **174**, 1144 (1954).
 211. STIMSON, M. M. AND O'DONNELL, M. J., "The Infrared and Ultraviolet Absorption Spectra of Cytosine and Isocytosine in the Solid State," *J. Am. Chem. Soc.*, **74**, 1805 (1952).
 212. SCHIEDT, U. AND REINWEIN, H., "On the Infrared Spectroscopy of Amino Acids. I. A New Preparation Technique for Infrared Spectroscopy of Amino Acids and Other Polar Compounds," *Z. Naturforsch.*, **7b**, 270 (1952).
 213. SCHIEDT, U., "On the Infrared Spectroscopy of Amino Acids. II. An Improvement on a Preparation Technique for the Infrared Photometric Determination of Amino Acids and Other Polar Compounds," *Z. Naturforsch.*, **8b**, 66 (1953).
 214. FORD, M. A. AND WILKINSON, G. R., "The Preparation and Properties of Pressed Alkali Halide Disks with Special References to Their Use in Spectroscopy," *J. Sci. Inst.*, **31**, 338 (1954).
 215. FORD, M. A., WILKINSON, G. R. AND PRICE, W. C., "The Pressed Disk Technique in Spectroscopy," Institute of Petroleum, London, 1955 p. 82.
 216. VON DIETRICH, H., "A Convenient Method of Pre-treating Potassium Bromide to be Used as Carrier Substance in Infrared Spectroscopy," *Z. Naturf.*, **11b**, 175 (1956).
 217. MORGAN, H. W., "A Leveling Device for Alkali Halide Pressed Disk Preparation," *Applied Spec.*, **13**, 48 (1959).
 218. MITZNER, B. M., "A Simple Sample Measuring Device for Use with the KBr Technique as Applied to Infrared Spectroscopy," *Appl. Spect.*, **10**, 75 (1956).
 219. MITZNER, B. M., "Gelatin Capsules for Potassium Bromide Infrared Technique," *Anal. Chem.*, **28**, 1801 (1956).
 220. CLARK, D. A. AND BOER, A. P., "A Method of Mounting Micro Samples in Infrared Spectrometry," *Spectrochim. Acta*, **12**, 276 (1958).
 221. BISSETT, F., BLUEM, A. L. AND LONG, L., JR., "Novel Micro and Semimicro Pelleting Technique for Infrared Spectroscopy," *Anal. Chem.*, **31**, 1927 (1959).
 222. LONGWORTH, R. AND MORAWETZ, H., "Measurement of the Infrared Spectra of Solids at Varying Temperatures by the Pressed Alkali Halide Disk Technique," *Chem. and Ind. (London)*, **1955**, 1470.
 223. BENT, H. A. AND CRAWFORD, B., JR., "Infrared Investigation of the Thermal Decomposition of di-t-Butyl Peroxide and Nitrate Esters in Potassium Halide Pressed Discs, and the Spectrum of Carbon Dioxide at High Pressures," *J. Am. Chem. Soc.*, **79**, 1793 (1957).
 224. BROWNING, R. S. WIBERLEY, S. E. AND NACHOD, F. C., "Application of Infrared Spectrophotometry to Quantitative Analysis in the Solid Phase," *Anal. Chem.*, **27**, 7 (1955).
 225. KIRKLAND, J. J., "Quantitative Application of Potassium Bromide Disk Technique in Infrared Spectroscopy," *Anal. Chem.*, **27**, 1537 (1955).
 226. SCHWARZ, H. P., CHILDS, R., DREISBACH, L. AND MASTRANGELO, S. V., "Quantitative Infrared Spectroscopy of Desoxyribonucleic Acid in the Fractional Milligram Range," *Science*, **123**, 328 (1956).
 227. WIBERLEY, S. E., SPRAGUE, J. W. AND CAMP-

INFRARED SPECTROPHOTOMETRY

- BELL, J. E., "Quantitative Infrared Analysis of Solids in Potassium Bromide Using an Internal Standard," *Anal. Chem.*, **29**, 210 (1957).
228. KIRKLAND, J. J., "Infrared Spectrophotometric Analysis of Fractional Milligram Quantities of Solids," *Anal. Chem.*, **29**, 1127 (1957).
229. NICHOLSON, D. E., "Quantitative Analysis of Mono- and Polybasic Benzene Carboxylic Acids in Potassium Bromide Disks by Infrared Spectroscopy," *Anal. Chem.*, **31**, 519 (1959).
230. BARKER, S. A., BOURNE, E. J., NEELY, W. B., AND WHIFFEN, D. H., "Infrared Spectra of Carbohydrates. V. Use of Potassium Bromide Films," *Chem. and Ind.*, 1418, (1954).
231. PLISKIN, W. A. AND EISCHEMS, R. P., "The Effect of Using the Pressed Salt Technique to Obtain the Spectrum of Chemisorbed Ammonia," *J. Phys. Chem.*, **59**, 1156 (1955).
232. FARMER, V. C., "Pressed-Disk Technique in Infrared Spectroscopy," *Chem. and Ind.*, 586 (1955).
233. KETELAAR, J. A. A., HAAS, C. AND VAN DER ELSKEN, J., "Infrared Absorption Spectra of Bifluorides in Alkali Halide Disks. The Formation of Mixed Crystals," *J. Chem. Phys.*, **24**, 624 (1956).
234. BROCKMANN, H. AND MUSSO, H., "Infrared Spectra of Optically Active Amino Acids and Their Racemates," *Chem. Ber.*, **89**, 241 (1956).
235. BAK, B. AND CHRISTENSEN, D., "Difficulties in the Infrared Spectrophotometric Identification and Estimation of Pure Compounds and Mixtures by Use of the Potassium Bromide Disk Technique," *Acta Chem. Scand.*, **10**, 692 (1956).
236. BARKER, S. A., BOURNE, E. J., WEIGEL, H. AND WHIFFEN, D. H., "Infrared Spectra of Carbohydrates. VI. Avoidance of Spectral Changes with Potassium Bromide Films," *Chem. and Ind.*, 318 (1956).
237. JONES, L. H. AND CHAMBERLAIN, M. M., "Formation of Mixed Crystals in the Use of the Alkali-Halide Disk Technique for Preparing Samples of $\text{KAu}(\text{CN})_2$ for Infrared Spectra," *J. Chem. Phys.*, **25**, 365 (1956).
238. BURNS, J. H. AND BREDIG, M. A., "Transformation of Calcite to Aragonite by Grinding," *J. Chem. Phys.*, **25**, 1281 (L) (1956).
239. TOLK, A. AND VAN DER MOLEN, H. J., "The Effect of Preparation Technique on the Infrared Spectrum of Benzoic Acid," *Chem. Weekbl.*, **53**, 656 (1957).
240. PADGETT, W. M. II, TALBERT, J. M. AND HAMNER, W. F., "Effects in the Solid State Infrared Spectrum of Cyanuric Acid," *J. Chem. Phys.*, **26**, 959 (1957).
241. SMAKULA, E., GORI, A. AND WOTIZ, H. H., "Effects of Polymorphism and Influence of Sample Preparation on the Infrared Spectrum of Estradiol-17 β ," *Spectrochim. Acta*, **9**, 346 (1957).
242. FARMER, V. C., "Effects of Grinding During the Preparation of Alkali-Halide Disks on the Infrared Spectra of Hydroxy Compounds," *Spectrochim. Acta*, **8**, 374 (1957).
243. STEWART, J. E., "Infrared Absorption Spectra of Urea, Thiourea, and some Thiourea Alkali Halide Complexes," *J. Chem. Phys.*, **26**, 248 (1957).
244. BAKER, A. W., "Solid State Anomalies in Infrared Spectroscopy," *J. Phys. Chem.*, **61**, 450 (1957).
245. ROBERTS, GLYN, "Alteration of Infrared Spectra of Steroids in Potassium Bromide," *Anal. Chem.*, **29**, 911 (1957).
246. MAKI, A. AND DECIUS, J. C., "Infrared Spectrum of Cyanate Ion as a Solid Solution in a Potassium Iodide Lattice," *J. Chem. Phys.*, **28**, 1003 (1958).
247. NORRIS, K. P. AND GREENSTREET, J. E. S., "Infrared Absorption Spectra of Casein and Lactose," *Nature*, **181**, 265 (1958).
248. MELOCHE, V. W. AND KALBUS, G. E., "Anomalies in the Infrared Spectra of Inorganic Compounds Prepared by the Potassium Bromide Pellet Technique," *J. Inorg. and Nucl. Chem.*, **6**, 104 (1958).
249. DUYCKAERTS, G., "The Infrared Analysis of Solid Substances. A Review," *Analyst*, **84**, 201 (1959).
250. MILLER, F. A. AND WILKENS, C. H., "Infrared Spectra and Characteristic Frequencies of Inorganic Ions," *Anal. Chem.*, **24**, 1253 (1952).
251. MASON, W. B. AND SALVATORE, J., "Spurious Infrared Bands Due to Grinding Small Amounts of KBr in Mortars of Various Composition," Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1956, paper No. 154.
252. MILKEY, R. G., "Potassium Bromide Method of Infrared Sampling," *Anal. Chem.*, **30**, 1931 (1958).
253. PFUND, A. H., "Improved Infrared Polarizer," *J. Opt. Soc. Am.*, **37**, 558 (1947).
254. ELLIOTT, A., AMBROSE, E. J. AND TEMPLE,

- R., "The Polarization of Infrared Radiation," *J. Opt. Soc. Am.*, **38**, 212 (1948).
255. NEWMAN, R. AND HALFORD, R. S., "An Efficient, Convenient Polarizer for Infrared Radiation," *Rev. Sci. Instr.*, **19**, 270 (1948).
 256. MAKAS, A. S. AND SHURCLIFF, W. A., "New Arrangement of Silver Chloride Polarizer for the Infrared," *J. Opt. Soc. Am.*, **45**, 998 (1955).
 257. HARRICK, N. J., "Infrared Polarizer," *J. Opt. Soc. Am.*, **49**, 379 (1959).
 258. EDWARDS, D. F. AND BRUEMMER, M. J., "Polarization of Infrared Radiation by Reflection from Germanium Surfaces," *J. Opt. Soc. Am.*, **49**, 860 (1959).
 259. CHARNEY, E., "Dichroic Ratio Measurements in the Infrared Region," *J. Opt. Soc. Am.*, **45**, 980 (1955).
 260. MECKE, R. AND GREINACKER, E., "IR Spectroscopic Studies on Organic Polycrystalline Layers with Linearly Polarized Light," *Z. Elektrochem.*, **61**, 530 (1957).
 261. DELBOUILLE, L., "Crystallographic Data Obtained from the Investigation of Spectra of Benzophenone and Various Derivatives by the Use of Polarized Infrared Light," *Bull. Acad. Belg. Cl. Sci.* **42**, 388 (1956).
 262. ANDERSON, SCOTT, "Orientation of Methylene Blue Molecules Adsorbed on Solids," *J. Opt. Soc. Am.*, **39**, 49 (1949).
 263. SAUNDERS, R. A. AND SMITH, D. C., "Infrared Spectra and Structure of Hevea and Gutta Elastomers," *J. Appl. Phys.*, **20**, 953 (1949).
 264. SUTHERLAND, G. B. B. M. AND JONES, A. V., "The Application of Polarized Infrared Radiation to Problems in Molecular Structure. I. Polyisoprenes," *Disc. Faraday Soc.*, **9**, 281 (1950).
 265. LIANG, C. Y. AND KRIMM, S., "Orientation in Polyethylene Terephthalate Films," *J. Chem. Phys.*, **27**, 327 (1957).
 266. ROSENKRANTZ, H. AND ZABLOW, L., "Comparison of Infrared Absorption Spectra of Steroids Obtained on Solid Films and Mulls and in Solutions," *Anal. Chem.*, **25**, 1025 (1953).
 267. BETHELL, D. E. AND SHEPPARD, N., "The Infrared Spectrum and Structure of Boric Acid," *Trans. Faraday Soc.*, **51**, 9 (1955).
 268. STEWART, J. E., "Use of Partially Oriented Solid Samples and Unpolarized Radiant Energy in the Analysis of Infrared Absorption Spectra," *J. Chem. Phys.*, **23**, 986 (1955).
 269. KRUSE, K. M. M., "Use of Partially Oriented Samples and Unpolarized Radiation in the Analysis of Infrared Absorption Spectra of p-Dichlorobenzene," *J. Chem. Phys.*, **25**, 591 (1956).
 270. KARAGOUNIS, G. AND PETER, O., "The Infrared Spectrum of Organic Compounds in Thin Layers," *Z. Elektrochem.*, **61**, 1094 (1957).
 271. KARAGOUNIS, G. AND PETER, O., "The Infrared Spectra of Molecular Layers on Carrier Material," *Z. Elektrochem.*, **61**, 827 (1957).
 272. HOLIDAY, P., "A Method of Mounting Filamentous Materials for Spectroscopic Examination in the Infrared," *Nature*, **163**, 602 (1949).
 273. FORZIATTI, F. H. AND ROWEN, J. W., "Effect of Changes in Crystalline Structure on the Infrared Absorption Spectrum of Cellulose," *J. Research NBS*, **46**, 38 (1951).
 274. CAROTTI, G. AND DUSENBURY, J. H., "Effect of Drawing on the Infrared Dichroism of Nylon 66 Filaments," *Nature*, **178**, 162 (1956).
 275. CANNON, C. G., "Applications of Infrared Spectroscopy in Chemical Industry. Applications of IR Spectroscopy to Textile Problems," *Chem. and Ind.* (1957) 29.
 276. MALCOLM, B. R., "The Mounting of Fibres and Organic Crystals for Spectroscopy in the Near Infrared," *J. Sci. Instr.*, **35**, 423 (1958).
 277. FRASER, R. D. B., "Use of Fiber Specimens for Infrared Absorption Measurements," *J. Opt. Soc. Am.*, **48**, 1017 (L) (1958).
 278. PIMENTEL, GEORGE C., "Infrared Studies of Mixed Crystals; Naphthalene in Anthracene," *J. Chem. Phys.*, **19**, 1536 (1951).
 279. LAWSON, J. R. AND MORGAN, H. W., "Infrared Absorption Intensities of Ions in Solid Solutions," *Bull. Am. Phys. Soc.*, **4**, No. 6, 389 (1959).
 280. MAKI, A. AND DECIUS, J. C., "Vibrational Spectrum of Cyanate Ion in Various Alkali Halide Lattices," *J. Chem. Phys.*, **31**, 772 (1959).
 281. HROSTOWSKI, H. J. AND PIMENTEL, G. C., "Interpretation of the Infrared and Raman Spectra of Mixed Crystals," *J. Chem. Phys.*, **19**, 661 (1951).
 282. HIEBERT, G. L. AND HORNIG, D. F., "A New Tool for the Study of Crystalline Spectra," *J. Chem. Phys.*, **20**, 918 (1952).
 283. KAGARISE, R. E., "Spectroscopic Studies of the Soaps of Phenylstearic Acid. I. Infrared Absorption Spectra and the Hydrolysis of Soap Films," *NRL Report 4344*, April 9, 1954; *J. Phys. Chem.*, **59**, 271 (1955).
 284. MITZNER, B. M., "Infrared Absorption Cell

- for the Study of Heterogeneous Reactions," *J. Phys. Chem.*, **60**, 1670 (1956).
 285. JANZ, G. J. AND DANYLUK, S. S., "An Infrared Cell Assembly for Volatile Solids," *Appl. Spect.*, **13**, 48 (1959).
 286. ROBINSON, T. S. AND PRICE, W. C., "The Interpretation and Use of Infrared Reflection Spectra," *Molecular Spectroscopy*, Institute of Petroleum, London, p. 211, (1955).
 287. RAPPAPORT, G., "Specular Infrared Spectral Reflectance for the Analysis of Organic Materials," *Phys. Rev.*, **74**, 115 (1948).
 288. PFUND, A. H., "The Identification of Gems," *J. Opt. Soc. Am.*, **35**, 611 (1945).
 289. BARCHIEWITZ, P., "Experimental Devices for Use with Prism and Grating Spectrographs," *Rev. Opt. (Theor. Instrum.)*, **33**, 518 (1954).
 290. JACQUEZ, J. A., MCKEEHAN, W., HUSS, J., DIMITROFF, J. M., AND KUPPENHEIM, H. F., "An Integrating Sphere for Measuring Diffuse Reflectance in the Near Infrared," *J. Opt. Soc. Am.*, **45**, 781 (1955).
 291. FRANCIS, S. A. AND ELLISON, A. H., "Infrared Spectra of Monolayers on Metal Mirrors," *J. Opt. Soc. Am.*, **49**, 131 (1959).
 292. STEWART, J. E. AND RICHMOND, J. C., "Infrared Emission Spectrum of Silicon Carbide Heating Elements," *J. Research NBS*, **59**, 405 (1957).
 293. REID, C. D. AND MCALISTER, E. D., "Measurement of Spectral Emissivity from 2μ to 15μ ," *J. Opt. Soc. Am.*, **49**, 78 (1959).
 294. MCALISTER, E. D., VILLA, J. J. AND SALZBERG, C. D., "Rapid and Accurate Measurements of Refractive Index in the Infrared," *J. Opt. Soc. Am.*, **46**, 485 (1956).
- Purification and treatment of complex samples*
(See also refs. 69, 103-107)
295. CHATTEN, L. G. AND LEVI, L., "An Infrared Study of the Reaction of Barbiturates with p-Nitrobenzyl Chloride," *Appl. Spect.*, **11**, 177 (1957).
 296. CHILDERS, E. AND STRUTHERS, G. W., "Infrared Evaluation of Sodium Salts of Organic Acids," *Anal. Chem.*, **27**, 737 (1955).
 297. ERLEY, D. S., "2,2-Dimethoxypropane as a Drying Agent for Preparation of Infrared Samples," *Anal. Chem.*, **29**, 1564 (1957).
 298. LIBERTI, A., COSTA, G. AND PAULUZZI, E., "Applicability of the Infrared Spectrophotometer as Analyzer in Gas Chromatography," *Chimica e Industria*, **38**, 674 (1955).
 299. BELLIS, H. E. AND SLOWINSKY, E. J., JR., "Application of Vapor Chromatography to Infrared Spectroscopy of Liquids," *J. Chem. Phys.*, **25**, 794 (1956).
 300. YVES, R. N., "On the Analysis of Rose Oils by Vapourphase Partition Chromatography and by Infrared Spectroscopy," *Perfumery and Essential Oil Record*, **49**, 290 (1958).
 301. KARR, C., JR., BROWN, P. M., ESTEP, P. A. AND HUMPHREY, G. L., "Analysis of Low-Temperature Tar Phenols Boiling up to 234°C ," *Fuel*, **37**, 227 (1958).
 302. HASLAM, J. AND JEFFS, A. R., "Applications of Gas-Liquid Chromatography. The Examination of Solvents from Plastic Adhesives," *Analyst*, **83**, 455 (1958).
 303. NAVES, Y. R., "Investigation and Determination of Cis Anethole in Essential Oils and in the Preparation of Anethole," *Compt. Rend.*, **246**, 1734 (1958).
 304. GALLAWAY, W., JOHNS, T., TIPOTSCH, D. G. AND ULRICH, W. F., "Microinfrared-Gas Chromatography Techniques as Applied to Complex Organic Systems," Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1958, paper no. 111.
 305. ANDERSON, D. M. W., "Applications of Infrared Spectroscopy. The Identification and Determination of Gas-Chromatographic Fractions," *Analyst*, **84**, 50 (1959).
 306. STEWART, J. E., BRACE, R. O., JOHNS, T. AND ULRICH, W. F., "Microquantitative Infrared Analysis. Application to Gas Chromatographic Fractions," *Nature*, **186**, 628 (1960).
 307. GRASSELLI, J., "Analysis by Combined Infrared Gas Chromatography Techniques," Cleveland Section, SAS, May 1959; MSG Meeting (Dow Chemical, Midland) Oct. 1958.
 308. JOHNS, T., BURNELL, M. R. AND CARLE, D. W., "Selected Applications with a New Preparative Gas Chromatograph," Instrument Soc. of Am. Proceedings, **2**, 82 (1959). (International Gas Symposium, June 1959).
 309. MEINSCHIEIN, W. G. AND KENNY, G. S., "Analyses of a Chromatographic Fraction of Organic Extracts of Soils," *Anal. Chem.*, **29**, 1153 (1957).
 310. LINNIG, F. J. AND STEWART, J. E., "A Spectroscopic Study of Oils Used in Oil-Extended Rubber," *J. Research NBS*, **59**, 27 (1957).
 311. STEWART, J. E., "Infrared Spectra of Chromatographically Fractionated Asphalts," *J. Research NBS*, **58**, 265 (1957).

312. DOBRINER, K., LIEBERMAN, S., RHOADS, C. P., JONES, R. N., WILLIAMS, V. Z., AND BARNES, R. B., "Steroid Metabolism. III. The Application of Infrared Spectrometry to the Fractionation of Urinary Keto-steroids," *J. Biol. Chem.*, **172**, 297 (1948).
313. RESNIK, F. E., HARROW, L. S., HOLMES, J. C., BILL, M. E. AND GREENE, F. L., "Infrared Micro Techniques for Identification of Carbohydrates and Other Organic Compounds," *Anal. Chem.*, **29**, 1874 (1957).
314. BARD, C. C., PORRO, T. J. AND REES, H. L., "Quantitative Infrared Determination of Trace Impurities in Solids Using Fractional Crystallization Technique. Determination of Catechol and Resorcinol in Hydroquinone," *Anal. Chem.*, **27**, 12 (1955).
315. PEAKER, F. W. AND ROBB, J. C., "A New Method of Fractionating High Polymers," *Nature*, **182**, 1591 (L) (1958).
316. PHILLIPPE, R. J. AND HOBBS, M. E., "Some Components of the Gas Phase of Cigarette Smoke," *Anal. Chem.*, **28**, 2002 (1956).
317. OSBORNE, J. S., ADAMEK, S. AND HOBBS, M. E., "Some Components of Gas Phase of Cigarette Smoke," *Anal. Chem.*, **28**, 211 (1956).

JAMES E. STEWART

SOLIDS IN POTASSIUM BROMIDE

The analysis of solids by infrared absorption studies has been greatly simplified with the advent of the potassium bromide technique. In this method the solid is intimately mixed with potassium bromide and then pressed in a die under high pressure. The resulting discs are visually clear and yield excellent absorption spectra of the solid material.

In April of 1952 Sisters Stimson and O'Donnell¹ published an article on the infrared and ultraviolet absorption spectra of cytosine and isocytosine in the solid state. In this paper they briefly described the potassium bromide technique. About the same time Schiedt of Max Planck Institute for Biochemistry in Tübingen, Germany, published information^{2, 3} regarding the method. Schiedt had investigated the method in detail including evaluation of such halide salts as NaCl, NaBr, KBr, KCl, and AgCl. He

also found potassium bromide to be most suitable of the halides studied.

Prior to these developments, the spectra of solids were obtained either by dissolving the sample in a suitable solvent and obtaining the spectrum of the solution or by mulling the sample with a mineral oil such as Nujol and measuring the spectrum of the mull. The spectra of waxes or low-melting solids were obtained by melting the solid on a rock salt window and allowing it to harden and then placing the window in the infrared spectrometer.

The solvent and Nujol mull methods were disadvantageous because of the lack of suitable solvents for many solids and because of the interference of either solvent or mineral oil bands. In addition the spectra obtained from mulls often had poorly resolved bands because of scattering losses by the mull. The mineral oil has strong absorption bands in the C—H stretching and bending regions at 3 and 7 microns. To obtain spectra in these regions a completely fluorinated material such as perfluorokerosene, or substances such as hexachlorobutadiene and polychlorotrifluoroethylene were substituted for the mineral oil. Quantitative analyses were carried out on Nujol mulls by adding an internal standard such as *D*-alanine,⁴ calcium carbonate,⁵ lead thiocyanate,^{6, 7} or naphthalene.⁸

Experimental Technique

Die Construction. There has been considerable work carried out on the dies involved in pellet preparation. At first it was thought necessary to have a die which could be evacuated so that entrapped air would not yield opaque spots in the window. Consequently vacuum dies of several types were designed by Schiedt. A commercial version of this die which used a split conical section to permit easy removal of the potassium bromide window has been described by Hausdorff.⁹ A modified vacuum die which presses a 3/8-inch diameter pellet directly into a 1-

inch ring has been described by Olsen.¹⁰ The vacuum does not have to be better than 15 mm Hg and can be obtained with an ordinary water aspirator; however, a mechanical pump will permit faster evacuation of the vacuum die and is preferable.

Unevacuable dies have been described by several authors.^{11, 12} Although reasonably clear discs of high transmittance can be obtained, they gradually become translucent as the entrapped air slowly reappears after pressure release. These dies were usually constructed to produce rectangular rather than circular windows. A drawing¹³ of such a die is shown in Figure 1. The main requirement for such a die is that the anvil and the plunger be of a good grade of hardened tool steel.

Recommended pressures are approximately 8 tons for a pressing time of five minutes and approximately 10 tons for a

pressing time of one minute. A Carver Laboratory Press of 10-ton capacity is suitable for pressing the potassium bromide. A simple press can also be economically constructed using an ordinary hydraulic truck jack and a suitable pressure measuring gauge.

Potassium Bromide. Only reagent grade potassium bromide is suitable. (The potassium bromide is usually ground, sieved through a 400-mesh screen and dried at 105°C. Scattered light is reduced to a minimum if the particle size of the solid is less than the shortest wavelength in the spectrum of the incident radiation, i.e., less than one micron. The potassium bromide should be stored at 105°C to prevent excessive water absorption. (Higher temperatures may cause decomposition and discoloration.) Potassium bromide of infrared quality, ground to the proper mesh, is commercially available from the Harshaw Chemical Company, Cleveland,

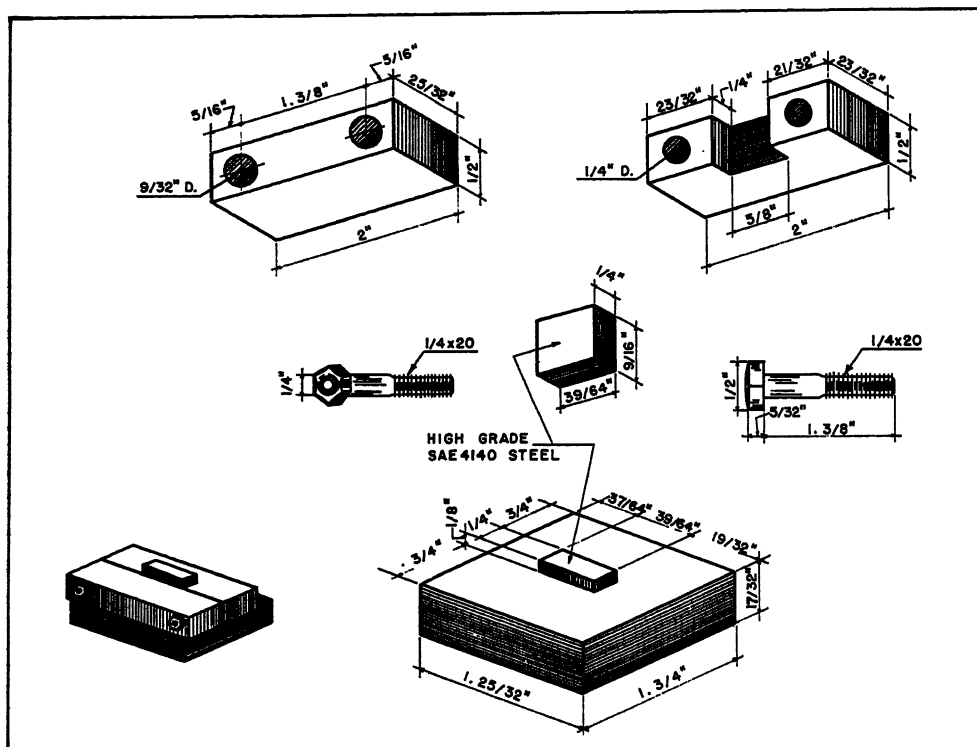


FIG. 1. Die for pressing potassium bromide pellets.

Ohio. The purity of the potassium bromide can be checked by measuring the infrared spectrum of a disc containing only potassium bromide. There should be only two weak bands, one at 3.0 microns (the O—H stretching vibration) and a smaller one at 6.1 microns (the O—H bending vibration), caused by small amounts of water. Although these two bands can be eliminated by drying the potassium bromide *in vacuo* and then pressing a window immediately from the dried powder, this technique is of little value because grinding of the dried potassium bromide, especially mechanical grinding, immediately contaminates the potassium bromide with adsorbed water. A typical bromide blank is shown in Figure 2.

Milkey¹⁴ has pointed out that severe grinding of the potassium bromide may produce strong absorption bands that could interfere with the spectrum of the sample. These absorption bands are attributed to some crystal alteration of the potassium bromide in the grinding process. Pellet blanks prepared from coarser powders (60 to 400-mesh) show small adsorbed water peaks and generally higher over-all transmittance readings than windows pressed from fine powders (greater than 400-mesh).

Sample Handling. To obtain suitable spectra the sample concentration may vary from less than 0.1% to as much as 3% in some aromatic compounds. It is difficult to predict the proper concentration but usually 0.5% is the best value for the initial

spectrum. Besides the concentration of the sample in the potassium bromide, equally important variables in obtaining good spectra are the particle size and the homogeneity of the sample in the potassium bromide matrix. A simple method for ensuring proper particle size and distribution is to grind the sample mechanically with a commercially available dental accessory known as a "Wig-L-Bug." This instrument was designed for preparing dental amalgams but it is equally satisfactory for mixing and grinding samples with potassium bromide. Either plastic or stainless steel capsules with a plunger can be used although the ground potassium bromide is more readily removed from the plastic capsule than the metal one.

The grinding time is very important. With the same concentration of sample in the potassium bromide the absorption bands increase in intensity as the grinding time is increased and finally reach a maximum and constant value usually in three to five minutes. The water bands at 3.0 and 6.1 microns also increase in intensity with the grinding time and are very intense if the sample is ground for as long as 10 minutes. If the potassium bromide window is left in the infrared beam or even standing in an air-conditioned room for an extended period of time, these bands decrease in intensity as the amount of adsorbed moisture decreases.

Another technique involves dissolving the sample in a volatile solvent, adding the solution to the potassium bromide, and then

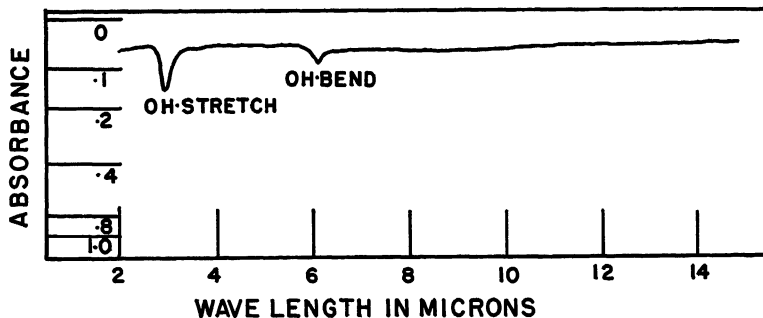


FIG. 2. Absorption spectrum of potassium bromide.

evaporating the solvent prior to grinding. Even water is suitable as a solvent since it is finally removed.

Freeze drying will provide good results but is a time consuming operation. If organic samples are rapidly cooled, submicroscopic crystals are produced. Solutions of weighed amounts of sample and potassium bromide can be cooled rapidly in an acetone "Dry Ice" mixture and the solidified mixture subjected to freeze drying. The resulting fluffy mixture can be dried over P_2O_5 at reduced pressure (approximately 10 mm) and slightly elevated temperature (50°C). Electron micrographs taken of such mixtures reveal small spherical particles with diameters as small as 0.01 to 0.05 micron.

Quantitative Analysis

Quantitative analysis with the potassium bromide technique can be carried out on substances which are not soluble. Studies^{11, 15} have proved that the plots of absorbance versus concentration or pellet thickness are linear, showing that Beer's law holds as well for materials dispersed in potassium bromide as for material dissolved in solution. The difficulty with this method is that the thickness of the potassium bromide pellet must be determined. Although the assumption can be made that if the same weight of potassium bromide is added to the die, the pellets will be of constant thickness,¹⁵ errors can occur. Measurements¹¹ on a number of pellets pressed under the same conditions were made to test the possibility that pellet weight might be a better measure of the sample in the infrared beam than the thickness. The average deviation of the mean was 6% in contrast to 4% for the same group on the basis of thickness.

The necessity for determining the sample thickness can be eliminated by incorporating an internal standard in the potassium bromide.¹⁶ This assumption is readily justified by consideration of Beer's law. The ab-

sorbance of the known material to be assayed at λ_k will be given by

$$A_k = a_k b c_k$$

and the absorbance of the internal standard at wavelength λ_s by

$$A_s = a_s b c_s$$

Now, dividing the first equation by the second,

$$\frac{A_k}{A_s} = \frac{a_k b c_k}{a_s b c_s}$$

the b 's cancel and because a_k and a_s are both constants at the wavelengths at which the measurements are made, and c_s , the concentration of the internal standard, is constant, these constants can be accumulated in an over-all constant, K , and

$$\frac{A_k}{A_s} = K c_k$$

Hence, a plot of A_k/A_s versus c_k will give a straight line. In this method it is not necessary to determine a_k and a_s , or even to know c_s exactly to obtain an empirical working curve.

For universal application in quantitative infrared work an internal standard should have a simple spectrum with a few sharp bands, be stable to heat and not absorb excessive moisture, be easily ground to a small particle size, be readily available, non-toxic, and yield clear potassium bromide pellets. Of all the materials investigated, potassium thiocyanate was the most suitable. With potassium thiocyanate as an internal standard, quantitative methods have been developed for the analysis of poly(vinyl chloride)-poly(vinyl acetate)-copolymers and for free fatty acid in aluminum soaps. Recently Frazer¹⁷ has recommended sodium azide as being superior to potassium thiocyanate as an internal standard. Sodium azide has a very strong peak at 2140 cm^{-1} and a weak peak at 1309 cm^{-1} . In the determination of sodium fluoroacetate in dried residues from

soil dispersion, sodium azide along with potassium bromide yielded Nujol mulls of medium absorbance values. The addition of the potassium bromide not only decreases the amount of Nujol required, thereby increasing the transmittance of the mull, but also facilitates the grinding of the solids before mulling.

Microsampling Techniques

One very important application of the potassium bromide technique involves the determination of spectra with as little as 5 micrograms of sample.¹⁸ These measurements cannot be made with the usual infrared spectrophotometer without some beam reducing device. Such systems employ all reflecting optics consisting of two precisely ground ellipsoidal condensing mirrors, and flat mirrors to divert the beam through the condensing mirrors and back into the monochromator. This method provides a sixfold reduction in beam size. About 12 % of the sample beam energy passes through the 0.5-mm hole provided for the micropellet. Energy balance between the two beams is obtained by means of a reference beam attenuator. The die for preparing the micropellets presses the pellet directly into the disc. Alloy inserts, composed of 10 % rhodium and 90 % platinum, form the working surfaces of both disc and anvil to lessen dangers of corrosion and sample contamination. Quantitative sample recovery is achieved by freezing 1 ml of an aqueous solution of potassium bromide in the form of a shell inside a lyophilization tube. The sample, dissolved in 1-2 ml of organic solvent, is then frozen in a thin layer inside the aqueous shell. The water and organic solvent are removed at a pressure of 0.07 mm Hg. The final KBr powder is mixed with a spatula and pressed directly. The spectra obtained with powders prepared by the lyophilization technique differ from those obtained by grinding. This difference has been attributed to the presence of microscopic crystals in the ground

powders. Hence, the so-called "sample degradation" caused by grinding can be explained by the progressive loss of crystallinity as the grinding proceeds.

Anomalies of the Potassium Bromide Technique

The many advantages of the potassium bromide technique have been stressed and it is equally important to mention a few of the disadvantages. In addition to the different spectra obtained with freeze drying or normal grinding techniques just reported, there have been differences found between the spectrum of a solid when measured in a Nujol mull as compared to its spectrum in potassium bromide. Several authors have reported changes in the spectra of solids in alkali discs caused either by metathesis^{19, 20} or the formation of mixed crystals.^{21, 22} Padgett²³ has discussed the different spectra obtained for cyanuric acid in potassium bromide, potassium chloride and a sublimed sample, and concluded that the effect is probably caused by ion interchange. Baker²⁴ has summarized solid state anomalies in infrared spectroscopy with emphasis on organic compounds. He lists the factors which influence the changes in pellet spectra as follows: (a) crystal energy of the organic phase, (b) total amount of energy used in grinding sample and matrix, (c) lattice energy of matrix, (d) particle size of matrix, (e) stress relaxation involving either the temperature of pellet or powder mixture or the time lapse between grinding the sample mixture and obtaining the spectrum, and (f) occurrence of polymorphic transitions.

As a specific example of the changes which can occur in potassium bromide, the following illustration can be cited. In the course of investigating potassium ferricyanide as a possible internal standard in potassium bromide,¹⁶ it was observed that the band at 2118 cm^{-1} decreased in intensity on grinding the sample and a new band appeared at 2029 cm^{-1} . This change was finally shown to be

caused by ferricyanide being converted to ferrocyanide on grinding. Judicious care must therefore be taken in interpretation of spectra obtained in potassium bromide, particularly if marked changes occur on grinding.

Although the potassium bromide technique has the limitations mentioned, it is still eminently suited for obtaining spectra of microsamples and amorphous polymers or resins. It should not displace the mineral oil mull technique but rather act as a complementary method. In combination, these two methods of obtaining spectra can yield more information about a sample than either one alone.

REFERENCES

1. STIMSON, M. M. AND O'DONNELL, M. J., *J. Am. Chem. Soc.*, **74**, 1805 (1952).
2. SCHIEDT, U. AND REINWEIN, H., *Z. Naturforsch.*, **7b**, 270 (1952).
3. SCHIEDT, U., *ibid.*, **8b**, 66 (1953).
4. BARNES, R. B., GORE, R. C., WILLIAMS, E. F., LINSLEY, S. G., AND PETERSON, E. M., *Ind. Eng. Chem., Anal. Ed.*, **19**, 620 (1947).
5. KUENTZEL, L. E., *Anal. Chem.*, **27**, 301 (1955).
6. WRIGHT, N., *Appl. Spectroscopy*, **9**, 105 (1955).
7. BRADLEY, K. S., AND POTTS, W. J., *ibid.*, **12**, 77 (1958).
8. CHILDERS, E., AND STRUTHERS, G. W., *Anal. Chem.*, **27**, 737 (1955).
9. HAUSDORFF, H., *Appl. Spectroscopy*, **7**, 75 (1953).
10. OLSEN, A. L., *Anal. Chem.*, **31**, 321 (1959).
11. BROWNING, R. S., WIBERLEY, S. E., AND NACHOD, F. C., *Anal. Chem.*, **27**, 7 (1955).
12. ROSENKRANTZ, H., POTVIN, P., AND SKOGSTROM, P., *ibid.*, **30**, 975 (1958).
13. MERRITT, P. E., Ph. D. thesis, Rensselaer Polytechnic Institute, 1954.
14. MILKEY, R. G., *Anal. Chem.*, **30**, 1931 (1958).
15. SUSI, H. AND RECTOR, H. E., *ibid.*, **30**, 1933 (1958).
16. WIBERLEY, S. E., SPRAGUE, J. W., AND CAMPBELL, J. E., *ibid.*, **29**, 210 (1957).
17. FRAZER, R. T. M., *ibid.*, **31**, 1602 (1959).
18. MASON, W. B., *The Perkin-Elmer Instrument News*, Vol. 10, No. 1, 1 (1958).
19. PLISKIN, W. A., AND EISENBERG, R. P., *J. Phys. Chem.*, **59**, 1156 (1955).
20. KETELAAR, J. A. A., HAAS, C., AND ELSKEN, J. VAN DER, *J. Chem. Phys.*, **24**, 624 (1956).
21. FARMER, V. C., *Chemistry and Industry*, 586 (1955).
22. JONES, L. H. AND CHAMBERLAIN, M. M., *J. Chem. Phys.*, **25**, 365 (1956).
23. PADGETT, W. M., II, TALBERT, J. M., AND HAMNER, W. F., *J. Chem. Phys.*, **26**, 959 (1957).
24. BAKER, A. W., *J. Phys. Chem.*, **61**, 450 (1957).

STEPHEN E. WIBERLEY

STEROL ANALYSIS (COMPARED WITH X-RAY DIFFRACTION AND COLORIMETRY)

Recent advances in the biochemistry of sterols have necessitated new methods for the qualitative and quantitative determination of these substances in extracts derived from biological materials. Spectrophotometry—both infrared and visual—and x-ray diffraction are the most promising of these methods. This study was made to compare the relative usefulness of infrared spectrophotometry, x-ray diffraction, and colorimetry in differentiating certain sterols.

The sterols chosen for this investigation were: cholesterol (Δ^5 -cholestene-3 β -ol), dihydrocholesterol (cholestane-3 β -ol), and β -sitosterol (Δ^5 -stigmastene-3 β -ol), their digitonides and mixtures of the sterols. The interrelationships of these substances in cholesterol metabolism make them of special interest at this time.

Methods and Instruments

Preparation and Purification of Sterols, Digitonides, and Mixtures. The sterols used in this study were purified as follows: a sample of the compound was dissolved in a minimum volume of ethyl alcohol over a steam bath. Water was then added until the solution became cloudy. Boiling temperature was maintained while a sufficient amount of solvent was added to redissolve the precipitate. The compound was allowed to crystallize at room temperature. The purity of the sterols was established by checking the melting points.

Digitonide derivatives of the purified

sterols were prepared by the addition of a saturated solution of digitonin in 50 % ethyl alcohol to an alcoholic solution of the sterol. The digitonides were allowed to stand at room temperature overnight, to ensure complete precipitation.

Two types of mixtures were prepared from the purified sterols: physical and recrystallized. The mixtures of cholesterol with dihydrocholesterol and of cholesterol with β -sitosterol had the following percentage compositions: 95-5, 75-25, 50-50, 25-75, and 5-95. The physical mixtures were prepared by grinding together the indicated amounts of the sterols using an agate mortar and pestle. To prepare the recrystallized mixtures, the component sterols were dissolved in ethyl alcohol and crystallized by the method described above. The percentage composition of the mixtures was checked by colorimetric analysis.

Infrared Spectrophotometry. Infrared absorption spectra were determined with a Perkin-Elmer Model 21 infrared spectrophotometer. The samples of purified sterols and their mixtures were made up to 0.04 molar solutions with carbon disulfide, and measured over the frequency range 1400 to 650 cm^{-1} . Digitonide samples were prepared by thoroughly mixing one mg of the digitonide with 800 mg of infrared quality potassium bromide. 500 mg of this mixture was placed in a Perkin-Elmer potassium bromide die, and pellets formed under a pressure of 23,000 psi for 2 minutes. The pellets measured 1.37 mm in thickness.¹ These samples were measured over the frequency range 1750 to 650 cm^{-1} .

X-ray Diffraction. For x-ray diffraction analysis, samples of purified sterols and sterol digitonides were powdered to 200 mesh and mounted in plastic capillaries.¹ The mounted specimens were exposed for 30 hours to vanadium-filtered chromium x-ray radiation in Norelco (North American Philips Co., Inc.) 114.9 mm Debye-Scherrer cameras. Eastman no-screen x-ray film was

used. The x-ray tube was operated at 35 KV potential and a current of 10 ma.

X-ray diffraction studies of the mixtures of cholesterol with dihydrocholesterol or with β -sitosterol were made with a recording diffractometer (Philips Electronics Inc.), fitted with a rotating specimen cup. Samples were ground to 200 mesh and placed in the diffractometer cups which were filled to the top surface. This required about 300 mm^3 , or 300 mg of powder. Loss of powder during rotation was prevented by placing a $\frac{1}{2}$ -mil sheet of plastic over the specimen surface. Chromium x-ray radiation, filtered by vanadium, was used for the diffractometer runs. The chromium tube was operated at 35 KV and 12 ma. Since the strongest lines of the purified sterols fell in the region 20 to 30° 2 θ , this range was used for scanning the mixtures.

Colorimetry. Visual absorption measurements of the sterol mixtures were made with a Klett-Summerson photoelectric colorimeter. For these determinations, the sterol mixtures were dissolved in acetic acid. All solutions had a concentration of 0.1 mg per cc.

Two colorimetric methods were used:

(I) A differential method was used for assaying the mixtures of cholesterol with dihydrocholesterol. In this method,² total sterols (A) were measured by the color reaction of anthrone with sterol digitonides in the presence of sulfuric acid (670 $\text{m}\mu$). Cholesterol (B) in these mixtures was determined by the Lieberman-Burchard reaction (620 $\text{m}\mu$). It follows that the concentration of such a sterol as dihydrocholesterol, which gives no color as a result of the Lieberman-Burchard reaction, is equal to (A) minus (B).

(II) The colorimetric method used for the assay of cholesterol and β -sitosterol mixtures depends on the fact that β -sitosterol and cholesterol have different absorption coefficients in the Lieberman-Burchard reaction. A standard curve was prepared by plotting

absorbancy of pure cholesterol and β -sitosterol, and mixtures of these substances. The percentage composition of unknown mixtures was determined by the use of this standard curve.

Discussion

The assay of mixtures of sterols like those found in biological extracts may be approached by applying methods used in both the qualitative and quantitative determination of individual sterols. It has been shown¹ that because of the similarity of the spectra, infrared absorption spectrophotometry is not entirely satisfactory for the qualitative identification of the commonly occurring sterols. This is especially true in the case of cholesterol and β -sitosterol which have absorption patterns that are identical even in the smallest detail. While other sterols differ somewhat in the details of their spectra, in many cases these differences are insufficient for positive differentiation and/or identification.

X-ray diffraction, on the other hand, yields powder patterns which differ sufficiently to permit the positive identification of a given sterol. However, certain precautions must be observed in the use of powder patterns for this purpose, since a number of sterols can crystallize in more than one system and thus yield more than one pattern for the same substance. Since the crystalline form is determined by the solvent and crystallization conditions, standardization of procedure is necessary to obtain reproducible results.

While both infrared spectrophotometry and x-ray diffraction offer possibilities for the quantitative determination of single sterols, these methods require highly complex and expensive instruments. Practical methods utilizing photoelectric colorimeters are available and used extensively. The majority of these are modifications of the Lieberman-Burchard reaction,³ and suitable for tentative identification and comparative analysis. They cannot be used for determination of a few of the sterols, including dihydrocholes-

terol, which do not yield a color in the Lieberman-Burchard reaction. For these substances quantitative infrared or x-ray diffraction methods are feasible.

In the isolation of β -sterols from biological samples, advantage is taken of the fact that these compounds form insoluble digitonides. While direct analysis of the sterol digitonides would simplify the determination of sterols in biological extracts, unfortunately all of the sterol digitonides investigated have identical infrared absorption spectra and x-ray diffraction powder patterns.¹ On the other hand, photoelectric colorimetry may be successfully applied to the digitonides, since the absorption spectra resulting from the reaction of these substances with the Lieberman-Burchard reagents are identical with the spectra of the corresponding sterols treated in the same way. An example of such a method is the differential determination of cholesterol and dihydrocholesterol in a mixture of their digitonides by colorimetric method (I) above.

In experimental work with sterols, mixtures rather than pure substances are the rule. In the investigation of mixtures by infrared spectrophotometry and x-ray diffraction, the procedure was to determine first if the spectra or diffraction patterns of the components were distinguishable in the mixture, and second to investigate the conditions under which a quantitative determination of the composition of the mixture might be possible.

The possibility of using infrared absorption spectrophotometry for analysis of mixtures depends on the components of the mixture. For example, mixtures of cholesterol and β -sitosterol cannot be assayed by this method, inasmuch as β -sitosterol and cholesterol possess almost identical absorption spectra in the infrared region. In the case of cholesterol and dihydrocholesterol mixtures, infrared spectrophotometry would appear to be applicable, since each sterol has specific spectral absorption bands. Unfortunately, because of the weakness of these bands, the

spectra of mixtures containing less than 25 % dihydrocholesterol or cholesterol cannot be distinguished from the spectra of the major component. It is clear that this method is not reliable qualitatively, and is useless from the quantitative point of view.

As applied to the analysis of sterol mixtures, x-ray diffraction was more effective than infrared spectrophotometry. The presence of all components was recognized in the patterns of physical mixtures. Furthermore, this method could be used to determine the composition of physical mixtures within 10 %, by using diffractometer calibration charts. The x-ray technique was inadequate for the analysis of crystallized mixtures of sterols. When dissolved, mixtures of sterols often crystallize as complex crystals,⁴ the pattern of which differs from that of the physical mixture of the same percentage composition. The formation of these complex crystals depends in an undetermined way on the percentage composition of the mixture. Therefore, until further studies have been completed, the use of x-ray diffraction for quantitative determination of mixtures—other than physical—is not recommended.

If the qualitative analysis of a sterol mixture has been determined by x-ray diffraction or some other method, in many cases it is possible to apply differential colorimetric analysis. Two such methods have already been mentioned in the section on colorimetry. By similar selective applications of absorption coefficients and colorimetric reagents, the quantitative analysis of mixtures of sterols is often possible.

REFERENCES

1. BEHER, W. T., PARSONS, J., AND BAKER, G. D., *Anal. Chem.*, **29**, 1147 (1957).
2. BEHER, W. T. AND ANTHONY, W. L., *J. Nutrition*, **52**, 519 (1954).
3. COOK, R. P. AND RATTRAY, J. B. M., in "Cholesterol Chemistry, Biochemistry, and Pathology," edited by R. P. Cook, Academic Press Inc., New York, 1958.

4. DAVIS, W. W., *Trans. N. Y. Acad. Sci.*, Ser. II, **18**, 123 (1955).

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VAPOR SPECTRA (INFRARED AND ULTRAVIOLET)

Absorption spectra of non-volatile substances are usually determined in the liquid or solid state.^{1, 2} The advantages of determining absorption spectra in the vapor state have not been made use of mainly because of the experimental difficulties involved in achieving accurate results. When measurements in the vapor state are needed for theoretical or analytical purposes, volatile liquids are handled quantitatively by pressure measurements. For compounds having volatilities of a few millimeters at room temperature, pressure measurements are difficult and are customarily avoided. These difficulties have been obviated simply by complete vaporization of precisely measured small volumes of liquid directly into an evacuated absorption cell. The technique is a modification of this laboratory's self-filling micropipet method of introducing minute liquid samples with high precision into a mass spectrometer.^{3, 4}

Experimental

Cell-filling Technique. The technique for quantitatively vaporizing liquids into a vacuum involves sampling with a capillary self-filling micropipet.^{3, 4} Mercury is poured into the barrel of the pipet containing the sample in order to seal the upper end; the pipet is touched to the sintered disc of the evacuated cell and the rubber tubing is used as a squeeze-bulb to squirt the sample and part of the mercury into the sintered disc.

Spectral measurements were made on a Perkin-Elmer Model 21 double-beam infrared spectrometer.

Some advantages of the quantitative

INFRARED SPECTROPHOTOMETRY

TABLE 1. ADVANTAGES OF QUANTITATIVE METHOD FOR VAPOR SPECTRA

1. Solvent interference is eliminated.
2. Fine structure of vapor-phase spectra facilitates qualitative analysis.
3. Quantitative analysis of multicomponent mixtures can be carried out.
4. Infrared vapor spectra of volatile compounds in aqueous solutions can be obtained.
5. Complex formation, such as hydrogen bonding and alcohol-aldehyde complexing is eliminated or diminished and the broad, masking absorption bands due to association are sharpened or eliminated.
6. Absorption-law deviations due to finite slit widths are rare. Absorption law tests are rapidly made by adding increments of sample to the cell.
7. Vapor pressures of a single component or of components in mixtures in the absorption cell can be calculated accurately without the use of vapor-pressure data.
8. Infrared pressure-broadening effects of mixtures of vaporized liquids can be studied quantitatively.
9. Vapor-phase reactions can be studied quantitatively. Reactants can be added easily to the reaction mixture at any stage.
10. The method is applicable to compounds of low volatility, since low vapor pressures are usable. A reliable spectrum is obtained in a one-meter cell from 0.45 mm. (calculated) of methanol vaporized from a 0.001-ml. pipet.

method of producing infrared vapor spectra are given in Table 1.

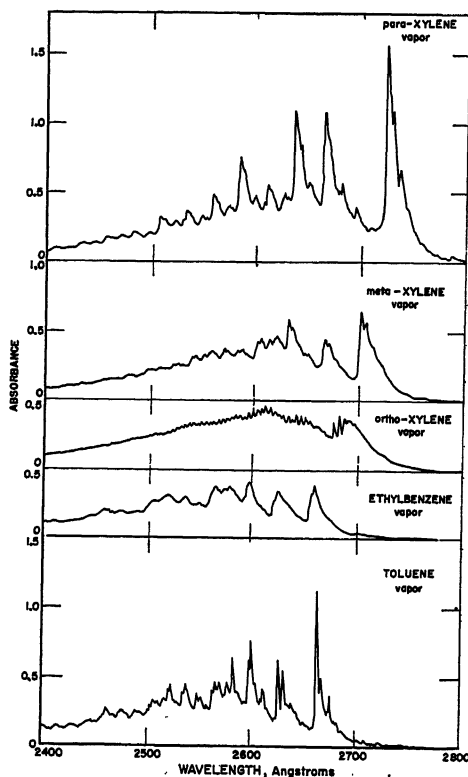
Disadvantages include pressure-broadening and sorption of the vapors of some compounds in the cell. Sorption difficulties can be minimized by prior conditioning of the system with the sample.

Qualitative Applications

Ultraviolet Vapor Spectra. The ultraviolet vapor spectra of several alkylbenzenes are shown in Figure 1. The fine structure compares favorably with the rather structureless solution spectra. The vapor spectrum of pyridine exhibits considerable fine structure that is qualitatively useful, but the 2-, 3-, and 4-methylpyridines have very little fine structure. The vapor spectrum of acetal-

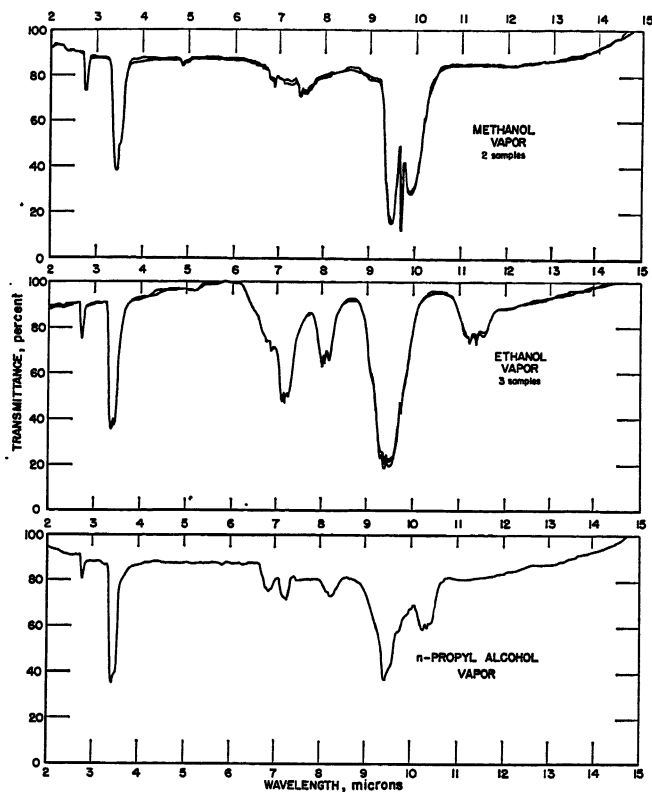
dehyde also has useful fine structure that is considerably decreased in the spectra of the higher homologs, propionaldehyde and butyraldehyde.

Infrared Vapor Spectra: Hydrogen-bond Dissociation. Vapor spectra in Figure 2 illustrate the advantageous production of fine structure and elimination of the broad absorption due to hydrogen-bonding customarily found in the spectra of alcohols in the liquid state. Hydrogen-bonded complexes show broad, ill-defined bands in the region of the hydroxyl stretching vibration. These broad bands may cover up a variety of bands due to different hydrogen vibrations, such as the sharp bands of free NH and OH groups. Furthermore, the vapor spectra of hydroxyl



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FIG. 1. Ultraviolet vapor spectra from 0.001 ml of aromatics vaporized in a 10-cm cell of 32.9 ml volume. Slit width 0.78 Å at 3000 Å.



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Fig. 2. Infrared vapor spectra, 0.008-ml pipet; 10 cm-cell.

compounds are free of the strong, ill-defined absorption at long wavelengths that occur in liquid spectra.^{5, 6}

Undesirable complexes from secondary reactions are formed in some systems. For example, liquid aldehyde and alcohol react to form hemiacetals. These are unstable entities with strong, characteristic spectra that interfere with analyses.⁷ In vapor-state spectra, such complexes can be avoided.

Quantitative Applications: Ultraviolet Spectra

The ultraviolet spectra in Figure 1 can be duplicated to within 0.01 absorbance unit, or to within 1 per cent by the liquid cell-filling technique. In a 10-cm. quartz cell with 32.9 ml. volume, the pressure of toluene pro-

duced at 25°C by 0.001 ml. of liquid is 5.3 mm. This pressure would be troublesome to measure with a reproducibility of 1 per cent.

Benzene and Toluene. Quantitative analyses were attempted with benzene-toluene mixtures. Intense absorption bands gave bad results because of deviations from the absorption law. Weaker bands gave fairly good results, although weaker bands entail somewhat lower sensitivity.

The apparent deviation from the absorption law may be due to finite slit widths or nearby stray radiation.⁸ Fluorescence of samples has been described as a possible source of such deviations in absorbance measurements on instruments that require the sample to be located between the exit slit and the detector,^{9, 10} but the possibility

of fluorescence interference was eliminated by a glass filter method.¹

C₈ Aromatics. Analyses of two blends of C₈ aromatics are shown in Table 2. Results for these 4-component blends are generally as good as solution analyses. Calibrations were carried out with 0.001 ml. of each liquid. The deviations from the absorption law were not as troublesome as with benzene and toluene.

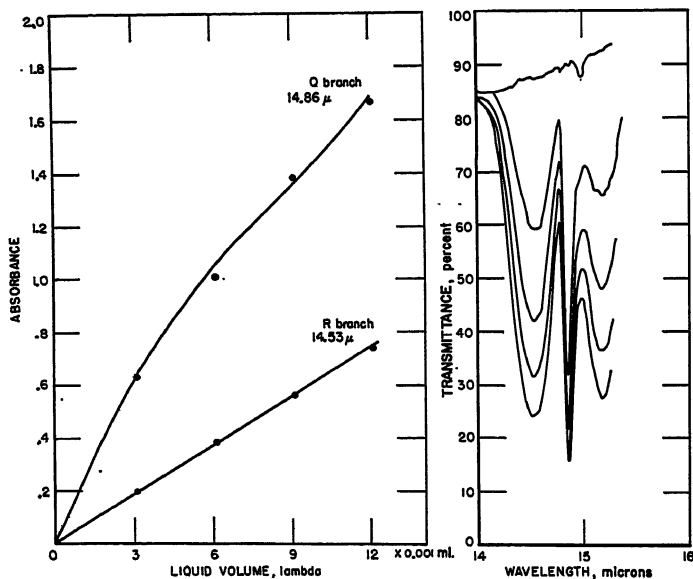
TABLE 2. ULTRAVIOLET ANALYSIS OF C₈ AROMATICS; 10 cm. CELL

Blend	λ , Å	Component	Volume-percent		
			Synthetic	Analysis	Difference
1	2706	<i>m</i> -Xylene	20.6	21.3	+0.7
	2691	<i>o</i> -Xylene	14.8	14.5	-.3
	2520	Ethylbenzene	15.1	14.3	-.8
	2585	<i>p</i> -Xylene	49.5	49.9	+.4
2	2706	<i>m</i> -Xylene	30.1	28.6	-1.5
	2691	<i>o</i> -Xylene	24.5	25.2	+.7
	2520	Ethylbenzene	21.7	21.4	-.3
	2585	<i>p</i> -Xylene	23.7	24.8	+1.1

Infrared Spectra

Absorption Law Deviations. The 14.8 micron band of benzene exhibits a very definite deviation from the absorption law in the liquid or solution states. In the vapor state (Fig. 3) this band is split into P, Q, and R branches; the Q branch is extremely sharp and shows the same deviation from linearity as in the liquid. But the R branch is linear; as the second strongest band in the spectrum, it is suitable for analytical use.

Pressure-broadening. The vapor-phase methanol band at 9.7 microns nearly obeys the absorption law in the 0.5 mm. range except for very slight self-pressure broadening. Vapor-phase analysis of methanol in the presence of water demonstrated a much larger pressure-broadening effect. The intensity of the PQR band at 9.7 microns increased almost linearly with incremental additions of water. Table 3 lists the Q-branch absorbance values for various volumes of water. The pressure-broadening effect of air on methanol was also large (Table 3). These data indicate the ease of



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FIG. 3. Infrared bands of benzene vapor in 1-meter cell; absorption law linearity tests for the 14.8 micron PQR band; 0.003 ml pipet.

studying pressure-broadening effects of normally liquid substances at low pressures.

Aqueous Solutions. Water as an infrared solvent is extremely troublesome. Because of the opacity of liquid water, permissible cell thicknesses are so small that quantitative applications are limited. In contrast to liquid water, the vapor is a comparatively weak absorber. Accurate analyses of aqueous solutions of volatile compounds are possible by the vapor technique. The only precaution required is that the partial pressure of water vapor be kept below the point of condensation. KBr cell windows can be used successfully.

Vaporized solutions of ethanol in water and methanol in water were investigated (see Table 4). The methanol band intensity was increased considerably by broadening due to water. Ethanol also showed slight evidence of pressure-broadening. These results indicate that aqueous solutions of a particular alcohol can be analyzed in the vapor state by means of an empirical calibration curve. The lower limit for analyses of methanol or ethanol in water in a one-meter cell is below one per cent.

Vapor-phase Reactions. The vapor technique is suitable for studying vapor-phase reactions. Incremental amounts of reactants may be added directly to the absorption cell without danger of losing part of the reactants or the products already in the cell. Mixing the reactants is a minor consideration because of the low pressures of the reactants.

Vapor-phase reactions of acetaldehyde and methanol were investigated. After acetaldehyde was added to the cell, small amounts of methanol were injected and the spectra recorded after each addition (Fig. 4). The distinctive hemiacetal bands that are found in the spectra of liquid mixtures of acetaldehyde and methanol did not occur in the vapor mixtures at low pressures. However, the acetaldehyde band at 11.0 microns was enhanced by methanol.

The dissociation of acetic acid has also

TABLE 3. PRESSURE BROADENING OF METHANOL 9.68 μ BAND BY AIR AND BY WATER

Water: (10-cm. cell)

Methanol liquid volume, ml.	Absorbance of methanol vapor	Volume of water, ml.	Absorbance of vapor, methanol and water
0.001	0.128	0.001	0.152
		.002	.172
		.003	.191

Air: (1-meter cell)

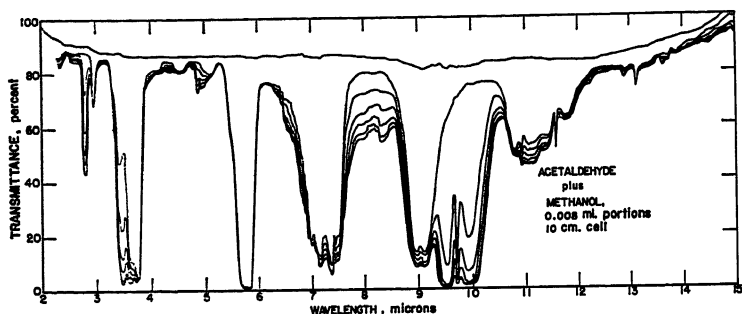
Methanol liquid volume, ml.	Absorbance of methanol vapor	Absorbance of methanol + 50 mm. air
0.001	0.085	—
.002	.157	0.260
.003	.219	.385
.004	.281	.497
.005	.354	.573

TABLE 4. VAPOR-PHASE INFRARED ANALYSIS OF ALCOHOLS IN WATER

Wavelength, μ	Component	Liquid volume, percent	
		Known	Found
<i>10-cm. cell</i>			
9.68	Methanol	33.3	48.0 ^a
	Water	66.7	
9.46	Ethanol	33.3	33.7
	Water	66.7	
<i>1-meter cell</i>			
9.46	Ethanol	3.3	4.4
	Water	96.7	
9.46	Ethanol	6.3	8.0
	Water	93.7	
9.46	Ethanol	16.7	19.6
	Water	83.3	
9.46	Ethanol	95.5	94.2
	Water	4.5	

* True analyses are obtainable with empirical calibration curves correcting for pressure broadening.

been studied by the present technique. The acetic acid bands that increase in relative intensity with decrease in sample pressure can be identified as bands due mainly to monomer. Correspondingly, bands that decrease in intensity with decreasing pressure



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Fig. 4. Infrared spectra of aldehyde vapor with increments of methanol added.

are attributable to dimer. This type of equilibrium may be studied quantitatively with high accuracy by means of the liquid-introduction method.

REFERENCES

1. FRIEDEL, R. A., AND QUEISER, J. A., *Anal. Chem.*, **29**, 1362 (1957).
2. FRIEDEL, R. A., *J. Appl. Spectroscopy*, **11**, 61 (1957).
3. FRIEDEL, R. A., SHARKEY, A. G., JR., AND HUMBERT, C. R., *Anal. Chem.*, **21**, 1572 (1949).
4. FRIEDEL, R. A., SHARKEY, A. G., JR., AND HUMBERT, C. R., Summary of Consolidated Engineering Corporation Group Meeting, New York, 1949.
5. STUART, A. V., AND SUTHERLAND, G. B. B. M., *J. Chem. Phys.*, **24**, 559 (1956).
6. YOUNG, C. W., *J. Opt. Soc. Am.*, **38**, 1095 (1958) (Abstract).
7. ASHDOWN, A., AND KLETZ, T. A., *J. Chem. Soc. (London)*, **1948**, 1454-56.
8. TUNNICLIFF, D. D., *J. Opt. Soc. Am.*, **45**, 963 (1955).
9. BRAUDE, E. A., FAWCETT, J. S., AND TIMMONS, C. J., *J. Chem. Soc.*, **1950**, 1019.
10. BRAUDE, E. A., AND TIMMONS, C. J., *Photoelectric Spectrometry Group Bull. No. 6*, p. 139 (1953).

R. A. FRIEDEL

MASS SPECTROMETRY

ANALYTICAL CHEMICAL APPLICATIONS

In recent years the mass spectrometer has developed into a versatile analytical instrument for qualitative and quantitative analysis as well as for molecular structure determination. A brief discussion of the theory of mass spectrometry is necessary to explain its use in an analytical laboratory.

When a compound in the vapor state is admitted to the evacuated ionization chamber of the mass spectrometer the molecules of the compound are bombarded by elec-

trons from a glowing tungsten filament. These electrons have sufficient energy to crack some of the molecules into fragments and ionize both the molecules and the fragments. The ions (usually only the positive ions) are accelerated to a desired kinetic energy into a magnetic field where they are separated into discrete ion beams according to their m/e (ratio of mass to charge). The ion beams can be detected individually on a collector plate by "sweeping" the ion beams past a slit in front of the collector plate. "Sweeping" is accomplished by varying the

magnetic field or the ion-accelerating voltage. The ion current to the ion-collector plate is amplified and recorded either photographically from galvanometers or on a strip chart recorder. The relative abundance of the ions is proportional to the relative ion beam intensities or to the "peak" heights on the photographic record or chart paper.

The mass spectrum of a compound consists of the masses (actually m/e) of the ion fragments produced in the ionization chamber and the relative abundance or "peak" heights of these ions. No two compounds will be cracked and ionized in exactly the same way, so no two compounds will have exactly the same mass spectrum. The mass spectrum is a "fingerprint" of a compound just as the infrared spectrum is. It is obvious from this that the mass spectrum can be used for qualitative identification of the compound.

Normally the pressure of a compound in the ion source of a mass spectrometer is about 10^{-4} mm. The temperature of the ion source is about 200°C . This puts a limit on the number of compounds that will give a mass spectrum. A mass spectrum can be obtained on only those compounds which, at the temperature of the ion source, have a vapor pressure of at least 10^{-5} to 10^{-4} mm. In reality the mass spectrometer is more limited than this. The construction of the spectrometer is such that the ionization chamber is continually pumped out. The sample to be analyzed, contained in a sample reservoir, is admitted continually into the ionization chamber through a small hole called a "leak." An equilibrium state between "leaking" in and pumping out of sample is reached almost immediately so that a constant pressure of replenished sample is maintained in the ionization chamber. The sample reservoir (usually about three liters in size) contains the sample at a pressure about 10 to 100 times as large as that in the ionization chamber. The sample reservoir pressure is normally about 0.05 mm. Therefore, the practical limit of obtaining a

mass spectrum is that the compound must have, at the temperature of the sample reservoir, a vapor pressure large enough to vaporize completely when introduced into the reservoir.

Auxiliary Equipment

Certain auxiliary equipment is almost a necessity for an analytical mass spectrometer. Some means must be available for measuring the sample size or pressure in the sample reservoir. The most convenient method of measuring sample pressure is with a micromanometer. A commercially available instrument for use on mass spectrometers will measure pressure in the range of 0–150 microns.

If the samples are gases at room temperature another method of measuring the pressure is also convenient. A small volume of the gas (about 3 ml) at a pressure of 50 mm (which can be measured on an ordinary mercury manometer) is expanded into the sample reservoir. If the reservoir volume is known the final pressure of gas in the reservoir can be calculated.

If the sample is a liquid it may be introduced into the sample reservoir with a micro-pipet or microsyringe. The volume introduced can be measured, and from the specific gravity the weight of sample introduced can be calculated.

The range of applicability of a mass spectrometer is greater if the temperature of the sample reservoir is higher. The simplest way of doing this is to enclose the reservoir in an oven. A temperature of 200°C is a good average temperature of operation. Materials of construction are critical when operating the reservoir at elevated temperatures. Usually glass and stainless steel are used in the reservoir and valves. Soft solder cannot be used at 200°C ; any metal joints would have to be silver-soldered. "Teflon" makes a good gasket material for valves and joints at this temperature.

With the heated reservoir (or sample sys-

tem) it is possible to obtain mass spectra on very high boiling and polar materials. At room temperature polar compounds absorb on the glass walls of the reservoir and give nonreproducible results. High boiling materials at room temperature might not have sufficient vapor pressure to give a mass spectrum.

Introduction of Samples

One problem in analyzing liquids and solids is that of introducing the materials into the evacuated sample reservoir without introducing air at the same time. The problem has been solved by several techniques.

Liquids can be introduced at room temperature through a mercury-covered, sintered glass disk on the reservoir.^{4, 14, 19} The tip of a micropipet of liquid is pushed through the mercury to touch the sintered glass disk. The low pressure in the reservoir draws the liquid out of the pipet and vaporizes it instantaneously.

A similar method is the one using a mercury sealed orifice.² The micropipet of liquid is inserted under the mercury into the orifice. The low pressure draws the liquid into the reservoir and vaporizes it. When mercury flows through the micropipet the pipet is removed and a glass rod with a rubber gasket is inserted in the orifice to seal off the mercury flow.

For elevated temperatures the sintered disk can be covered with gallium, which has a negligible vapor pressure even at 400°C. The micropipet can be used in the same way as it is for the mercury-covered, sintered disk. When solids melting below the reservoir temperature are to be run, the micropipet is filled with the molten compound. It will solidify in the pipet at room temperature, but when it is inserted in the hot gallium it will melt and be drawn into the reservoir.

A better method for introducing liquids into a heated sample system is to use a hypodermic needle through a self-sealing silicone

rubber diaphragm.²⁰ The liquid is drawn up into the needle the top end of which is sealed with a silicone plug; the other end is inserted through the silicone diaphragm. The high temperature and low pressure almost instantaneously vaporize the sample.

The best method of positive introduction of solid samples is by introducing the sample in a "Teflon" cup through a "Teflon"-sealed orifice.¹ The sample is put in a hole drilled in a "Teflon" slug. A solid slug is put on the open end of the sample slug and both are put in a split sleeve. The sleeve is placed upright on the "Teflon"-sealed orifice and a plunger is pushed down until the sample slug goes into the reservoir and the solid slug behind it seals off the orifice. The high temperature causes the solid to melt and vaporize.

Interpretation of Spectra

The mass spectrum of a mixture of compounds is merely the sum of the individual spectra of all the compounds with consideration of the mole fraction of each of the compounds. Any ion fragment of a compound can be used for the calculation of its concentration in a mixture, but usually an ion fragment (or peak) is picked that is characteristic of the compound and, if possible, without interference from peaks of the other compounds in the mixture.

"Sensitivities" for compounds are determined by dividing the peak height (ion current) for a characteristic ion fragment of the pure compound by the pressure of the compound in the reservoir. From this "sensitivity" and the peak height of the compound in the mixture spectrum the partial pressure (and mole per cent) of the compound in the mixture can be calculated.

Calculating compositions of mixtures is simple if the components of the mixture give spectra that do not mutually interfere at all their masses. If there are mono-component fragments for each compound, measurements of peak heights will, with simple

calculations using the sensitivities of the compounds, yield the mole per cent of each component.

If the mixture spectrum has no mono-component peaks, simultaneous equations must be used to calculate the contributions at characteristic peaks of each of the components. With twelve simultaneous equations, calculations for as many as twelve components can be easily performed with calculators.

The mass spectrum can be used to identify unknown compounds. The use in this case is very similar to the use of infrared spectra. A file of mass spectra of many compounds is necessary. The unknown spectrum is compared with the knowns. A method of sorting mass spectra to pick out the known spectra which match the unknown will expedite this technique. A good method of sorting spectra makes use of spectra coded on IBM cards.¹ The m/e of major fragments or peaks in the mass spectrum of a compound are punched on IBM cards. The IBM collator can select cards which have major peaks at the masses of the major peaks of the unknown. Simultaneously it rejects cards which have major peaks at the masses at which the unknown spectrum has no major peaks.

The mass spectrum will help greatly in elucidating the structure of a compound. Many articles have been published on the mass spectra of classes of compounds.^{5, 6, 7, 8, 10, 12, 13, 16, 17} Empirical formulas for major peaks in the spectra of compounds in certain classes have been worked out. The peaks in the spectrum of an unknown compound in a certain family of compounds can be used to determine the structure of the unknown compound.

The mass spectrum of a compound is determined by the stability of its bonds. In other words, cracking of a compound in the mass spectrometer will occur most abundantly at its weakest bond. This information will help in determining quite a bit about

the structure of the compound. For example, cracking will occur to a greater extent at a single bond than at a double bond, and to a greater extent at a double bond than at a triple bond.

Simplifying of Spectra

There are many techniques that can be used to concentrate a component (or components) in a mixture so that a more useable spectrum is obtained. This is a necessity when the component(s) of interest is (are) at too low a concentration to be detected or when the other components give interfering spectra. Distillation, solvent extraction, chromatography, and vapor phase chromatography are some of the common concentration methods used.

Ordinarily the mass spectrometer cannot be used for detecting components in a mixture in the parts per million range. But by special techniques organic impurities in the atmosphere can be detected in this concentration range.^{9, 15, 18} One rapid, simple method⁹ consists of collecting an air sample in a 50-ml glass bulb. The bulb is immersed in liquid nitrogen to condense all the condensible impurities and the non-condensibles, such as nitrogen, oxygen, argon, etc., are pumped off. The bulb is then warmed to room temperature, the contents admitted to the sample reservoir, and the mass spectrum scanned. Impurities in the range of 10 ppm are detectable.

This technique can be extended to a lower limit of detection. Increasing the sample bulb to a volume of 200 ml, decreasing the sample reservoir in size from 3 liters to 150 ml, and raising the filament emission current in the ion chamber by a factor of four lowers the limit of detection so that as little as 0.1 ppm of impurity can be detected in the atmosphere. Replacing the normal DC amplifier on the mass spectrometer with a vibrating reed electrometer increases sensitivity by a large factor (about 10-100). With the vibrating reed electrometer as little as 0.01

ppm of impurities can be detected in the atmosphere.

A recent technique for simplifying the spectrum of a mixture of compounds is low voltage mass spectrometry.³ The mass spectrum is obtained at an electron-accelerating voltage low enough so that no fragmentation of the molecule occurs. This essentially gives a spectrum of only one peak—that of the ion molecule. Obviously this simplifies the spectrum of a mixture of compounds and eliminates much mutual interference. For example, in a mixture of hydrocarbons it is possible to make a clean separation of the saturates and the unsaturates of a given C number.

A "natural" analysis by the mass spectrometer is that of nonvolatile materials for volatile components. Since the nonvolatile material will give no spectrum that will interfere, only the volatile components will show on the spectrum. This permits a large sample to be loaded into the spectrometer so that very small amounts of volatiles can be analyzed. The easiest way to introduce the sample into the reservoir is through a "Veeco" quick-vacuum coupling. This coupling with a "Teflon" "O" ring makes a vacuum-tight seal with a glass or metal tube. The sample is put in a glass bulb of suitable size with a neck to fit the coupling. The bulb is immersed in liquid nitrogen and the air is pumped out of the bulb. The liquid nitrogen is removed and bulb contents are allowed to warm up to reservoir temperature. The volatile components then can be scanned. Samples as large as 25 grams can be handled by this technique.

This same coupling can be used for introducing fractions from a vapor phase chromatography unit. Usually these fractions are collected as they come off the chromatography column into a U-tube immersed in liquid nitrogen. The U-tube is then inserted in the "Veeco" quick-vacuum coupling and the carrier gas pumped off while the U-tube is still in liquid nitrogen. The liquid nitrogen

is then removed and the U-tube and contents are allowed to warm up to reservoir temperature. The fraction vaporizes into the reservoir and its mass spectrum is scanned. This technique is very useful for identifying unknown peaks in a vapor phase chromatogram.

REFERENCES

1. CALDECOURT, V. J., *Anal. Chem.*, **27**, 1670 (1955).
2. Consolidated Engineering Corporation, *CEC Recordings*, June, 1949.
3. FIELD, F. H., AND HASTINGS, S. H., *Anal. Chem.*, **28**, 1248 (1956).
4. FRIEDEL, R. A., SHARKEY, A. G., JR., AND HUMBERT, C. R., *Ibid.*, **21**, 1572 (1949).
5. FRIEDEL, R. A., SHULTZ, J. L., AND SHARKEY, A. G., JR., *Ibid.*, **28**, 926 (1956).
6. FRIEDEL, R. A., SHULTZ, J. L., AND SHARKEY, A. G., JR., *Ibid.*, **28**, 940 (1956).
7. GILPIN, J. A., AND McLAFFERTY, F. W., *Ibid.*, **29**, 990 (1957).
8. GILPIN, J. A., *Ibid.*, **31**, 935 (1959).
9. HAPP, G. P., STEWART, D. W., AND BROCKMYRE, H. F., *American Industrial Hygiene Assoc. Quarterly*, **11**, 135 (1950).
10. JUDSON, C. M., AND FRANCEL, R. J., ASTM Committee E-14 on Mass Spectrometry, San Francisco, May, 1955.
11. McLAFFERTY, F. W., AND GOHLKE, R. S., ASTM Committee E-14 on Mass Spectrometry, New Orleans, May, 1954.
12. McLAFFERTY, F. W., *Anal. Chem.*, **29**, 1782 (1957).
13. MEYERSON, S., *Applied Spectroscopy*, **9**, 120 (1955).
14. PURDY, K. M., AND HARRIS, R. J., *Anal. Chem.*, **22**, 1337 (1950).
15. QUITMAN, E. R., METRO, S. J., AND LEWIS, J. B., *Ibid.*, **26**, 352 (1954).
16. SHARKEY, A. G., JR., SHULTZ, J. L., AND FRIEDEL, R. A., *Ibid.*, **28**, 934 (1956).
17. SHARKEY, A. G., JR., FRIEDEL, R. A., AND LANGER, S. H., *Ibid.*, **29**, 770 (1957).
18. SHEPHERD, M., ROCK, S. M., HOWARD, R., AND STORMS, J., *Ibid.*, **23**, 1431 (1951).
19. TAYLOR, R. C. AND YOUNG, W. S., *Ibid.*, **17**, 811 (1945).
20. WILKERSON, R. C., ASTM Committee E-14 on Mass Spectrometry, San Francisco, May, 1955.

R. BRUCE LEBLANC

ANOMALOUS BEHAVIOR OF *gem*-DIETHERS

Normally, the mass spectrum of a compound is considered a "fingerprint" of the compound if conditions such as temperature, focus, and type of scanning are held constant. Condition of the filament in the ion source usually does not appreciably alter the cracking pattern of a compound.

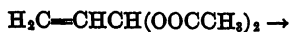
Gem-diethers (compounds with two alkoxy groups on the same carbon atom) are one class of compounds which do give different spectra, depending on whether the filament is bare tungsten or carbonized tungsten. The carbonized tungsten filament gives what can be called the normal spectrum of the compound. The uncarbonized tungsten filament causes partial decomposition of the *gem*-diether into a vinyl ether and an alcohol according to the equation:



The mass spectrum obtained under these conditions is a summation of the normal spectra of the *gem*-diether, the alcohol and the vinyl ether.

From the equation above it can be seen that the *gem*-diether must have a beta-hydrogen atom for this type of decomposition. Eight *gem*-diethers, five orthoesters (*gem*-triethers) and two cyclic *gem*-diethers were studied and the results were consistent with the above equation.

A *gem*-diester also exhibited a similar decomposition. The mass spectra of allylidene diacetate was obtained with a carbonized filament and an uncarbonized filament, and with the latter a decomposition was observed:



The exact cause of the anomalous spectra is not known. Two possible causes are (1) the uncarbonized tungsten catalyzes the decomposition of the *gem*-diethers, or (2) the higher operating temperature of the uncarbonized

tungsten filament decomposes the *gem*-diethers.

The mass spectrometers in most analytical laboratories are operated with carbonized filaments. This carbonization is accomplished by leaving a sample of hydrocarbon (isobutylene, styrene, etc.) in the sample reservoir for a long enough period of time to carbonize the filament.

This anomalous behavior of *gem*-diethers points up the need for carbonization to attain stability of the instrument. As the filament is carbonized the spectrum changes slowly from one of a mixture of compounds to the normal spectrum of the *gem*-diether. This reaction of *gem*-diethers can be used as a method of determining when a filament is sufficiently carbonized for stable operation of the spectrometer.

Note: This research was published in *Analytical Chemistry*. The reference is: LeBlanc, R. B., *Anal. Chem.*, **30**, 1797 (1958).

R. BRUCE LEBLANC

BENNETT RADIO FREQUENCY SPECTROMETER

The Bennett Radio Frequency Mass Spectrometer is a non-magnetic analyzer which separates ions of different charge to mass ratio. The usual spectrometer consists of single stage analyzer sections spaced to take advantage of the transit time methods of mass analysis. The single stage analyzer used by itself provides a low resolution method of mass analysis. A single stage RF mass spectrometer for positive ions is shown in Figure 1. It consists of three equally spaced plane parallel grids, 1, 2 and 3, called an analyzer stage, followed by a retarding potential grid 4 and an ion collector. The negative voltage V_A applied to all grids of the analyzer stage accelerates thermal positive ions from the ion source to a velocity v proportional to the square root of the charge-to-mass ratio as defined by the energy

equation:

$$W = eV_A = \frac{1}{2}mv^2 \text{ (ergs).}$$

When the ions enter the analyzer stage, the RF field created by the sinusoidal voltage V_{RF} applied to the center grid imparts incremental energy Δw to the ions as they pass through the stage. The amount of energy gained or lost depends on the time the ion spends between grids 1 and 3 and the phase of the RF cycle at the instant the ion crosses the center grid.

The principle of mass analysis by RF velocity selection states that ions of velocity v , which traverse a uniform radio frequency field ($\omega = 2\pi f$) between three parallel grids equally spaced a distance s , gain the maximum amount of energy from the field when the transit angle, $\alpha = s\omega/v$, between adjacent grids is 2.3311 radians and when the ion crosses the center grid as the field reverses at the transit angle of π radians. Ions which receive maximum energy are separated from ones receiving less than the

maximum by a retarding field. Those ions which overcome and pass through the retarding field reach a collector and are detected. The mass of the selected singly charged ion in Atomic Mass Units is

$$M = \frac{0.286 V_A \text{ volts}}{s^2 f^2}$$

where V_A is the potential in volts through which the ion has fallen, s is the spacing between adjacent grids in centimeters, and f the frequency in megacycles per second.

Features of the Bennett Radio Frequency Spectrometer which merit attention are its lightweight, simple construction, mass analysis without a magnetic field, ion beam cross section limited only by grid size, and linear mass to voltage relationship. In addition, the electronic circuits required to generate the potentials for the mass analyzer are not elaborate.

Although the mass resolution of a single stage RF spectrometer is insufficient for most applications, the theory provides the basic conditions for RF velocity selection and will be considered in detail.

Energy Gain

The equation for the energy gain Δw is

$$\Delta w = \Delta \left(\frac{mv^2}{2} \right) = v \Delta(mv) = v \int_0^t F dt \quad (1)$$

when the simplifying assumptions are made that the energy gained by the ion from the RF field is small compared to the energy acquired from the accelerating potential V_A , and that space charge effects are negligible. In Equation (1) F is the force on the ion of mass m while it is within the stage. In terms of a sinusoidal RF electric field between grids the force on an ion when it is between the first and second grid is

$$F_{12} = m\ddot{x} = Ee \sin(\omega t + \theta)$$

and between the second and third grid

$$F_{23} = m\ddot{x} = -Ee \sin(\omega t + \theta)$$

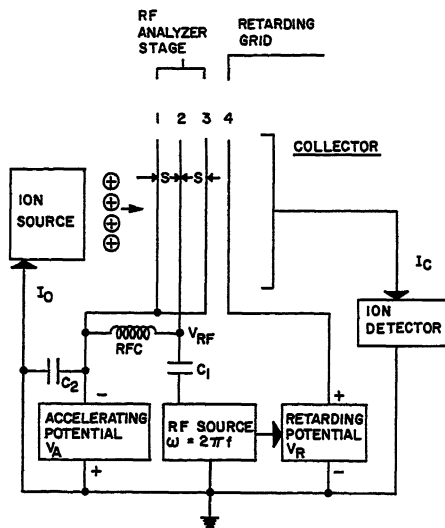


FIG. 1. Single stage RF mass spectrometer for positive ions. Grids 1-4 are of knitted tungsten mesh mounted on a support ring. The RF choke holds the RF analyzer grid at the accelerating potential V_A . C_1 couples RF energy to the center grid, and C_2 provides the RF ground for grids 1 and 3.

where θ is the phase angle of the sinusoidal oscillation at $t = 0$, E is the maximum RF field strength and e is the ionic charge. Time t is taken to be zero when the ion crosses the center grid.

Integrating Equation (1) with transit time limits of $-s/v$ and 0 for the time the ion is between the first and second grids, and 0 and s/v when it is between the second and third grids gives the energy gain of a single stage.

$$\begin{aligned} \Delta w &= v \left(\int_{-s/v}^0 E e \sin(\omega t + \theta) dt \right. \\ &\quad \left. + \int_0^{s/v} -E e \sin(\omega t + \theta) dt \right) \\ &= \frac{v E e}{\omega} [2 \cos \theta - \cos(-\alpha + \theta) \\ &\quad - \cos(\alpha + \theta)] \\ &= -2e V_{RF} \left[\frac{1 - \cos \alpha}{\alpha} \right] \cos \theta \text{ ergs} \end{aligned} \quad (2)$$

where $E = V_{RF}/s$ and $\alpha = s\omega/v$.

In electron volts the energy gain is

$$\begin{aligned} V(\alpha\theta) &= \frac{\Delta w}{e} = -2\sqrt{2} V_{RF_{rms}} \\ &\quad \cdot \left[\frac{1 - \cos \alpha}{\alpha} \right] \cos \theta \text{ volts} \end{aligned} \quad (2a)$$

Equation (2a) is plotted in three dimensional form in Figure 2. Energy $\Delta w/e$ is plotted on the vertical axis, in electron volts per volt of $V_{RF_{rms}}$; ion transit angle α is plotted on the horizontal axis; and the phase angle θ rotates about the transit angle axis. V_R , the horizontal plane perpendicular to the energy axis, represents the retarding potential level.

Optimum Phase and Transit Angle

By inspection Equation (2) has a maximum with respect to θ when

$$\cos \theta = -1, \quad (3)$$

or its first maximum when $\theta = \pi$. In terms of the ion passage through a stage,

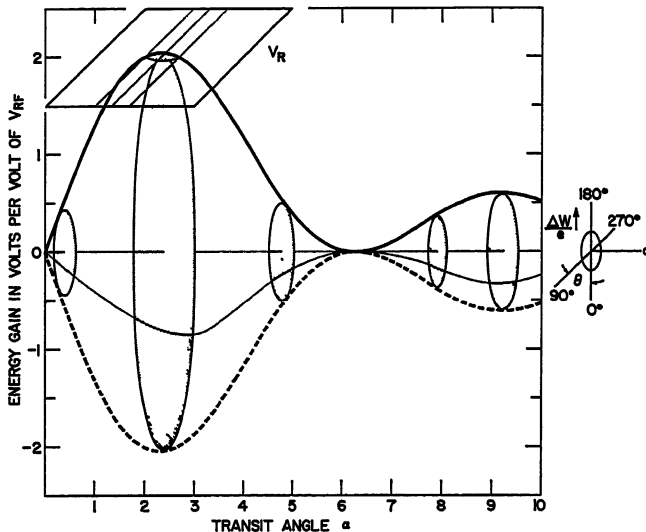


FIG. 2. Incremental energy $V(\alpha\theta) = \frac{\Delta w}{e}$ imparted to an ion in a single Bennett analyzer stage by an

RF voltage, V_{RF} , as a function of the ion transit time between adjacent grids, $\alpha = \frac{s\omega}{v}$, and the RF phase angle, θ . The horizontal plane V_R is the retarding potential level. The first maximum has a value of $2.05 V_{RF}$ and occurs at $\alpha_0 = 2.3311$, $\theta_0 = 180^\circ = \pi$ radians.

this means that in order to gain maximum energy from the field the ion must resonate with the field and pass the center grid when the field reverses direction at π radians. When this occurs the ion is pulled toward grid 2 by the field when it is between grids 1 and 2 and pushed away from grid 2 when it is between grids 2 and 3.

Substituting $\theta = \pi$ in Equation (2a) gives the maximum energy gained (in volts) by an ion in a single stage per volt of R.F. rms as a function of the ion transit angle α

$$V(\alpha)_{\theta=\pi} = \frac{\Delta w}{e} = 2\sqrt{2}V_{\text{RF rms}} \left[\frac{1 - \cos \alpha}{\alpha} \right]. \quad (4)$$

$V(\alpha)_{\theta=\pi}$ is plotted in Figure 2 as the solid curve. It shows that all ions satisfying Equation (3) gain energy from the field, and that the distribution is broad with the first maximum below π radians. The maximum occurs when the first derivative is zero, i.e.: $\alpha \sin \alpha + \cos \alpha - 1 = 0$. When graphically solved the first maximum occurs at

$$\alpha = s\omega/v = 2.3311 \text{ radians.}$$

The corresponding value for $V(\alpha)_{\text{max}}$ is 2.05 $V_{\text{RF rms}}$. These are the conditions for optimum R.F. velocity selection in the Bennett spectrometer.

Ions which pass the center grid at other than an R.F. phase angle of π radians gain less than the maximum energy or even lose energy to the field according to the value of $-\cos \theta$.

Integration of Equation (2) with respect to θ shows that for a uniform flow of ions to a stage the total energy given to all ions during an R.F. cycle is zero. This fact rules out detection of the selected ion by observing the average energy given to the ions by the R.F. source.

Mass of the Selected Ion

The mass of the ion receiving maximum incremental energy is obtained by eliminating v between the energy equation $eV_A = \frac{1}{2} M m_0 v^2$ and the optimum transit angle

$$\alpha = s\omega/v = 2.3311 \text{ to give}$$

$$M = \frac{0.266V_A}{s^2 f^2}. \quad (5)$$

M is the atomic mass number of the ion, m_0 the absolute mass of the hydrogen atom, V_A the total potential in volts through which the ion has fallen upon entering the analyzer. The quantity $0.266/s^2 f^2$ is the spectrometer proportionality constant in AMU/volt. Of the three independent variables, s , f , and V in Equation (5), only f and V are readily varied to cover a given mass range. For a given percentage change a frequency sweep covers a larger mass range in the inverse square relationship than does a change in V_A which produces a linear mass relationship. However, since the energy gain is a function of the R.F. voltage, the variable frequency sweep, unless amplitude stabilized, is seldom used. Sweeping V_A linearly has the advantage of a linear mass scale which can be generated by electronic or electromechanical means independent of the R.F. source.

Retarding Potential

In the previous sections equations for the incremental energy added to an ion as it passes through an R.F. analyzer stage and the mass of the ion receiving maximum energy were obtained. Thus as the ions exit from the analyzer they have $V_A + V(\alpha)$ volts of kinetic energy. V_A volts of the energy are lost as the ion decelerates in traversing the distance between grid 3 and the ground plane between grids 3 and 4. Of the remaining $V(\alpha)$ volts, it is the function of the positive retarding potential V_R applied to grid 4, Figure 1, to reject all ions except those which have gained more than V_R volts of energy. For example, if V_R is 97.5 % of the maximum gained, as represented by the horizontal plane in Figure 2, only ions whose transit angles are between 2.0 and 2.7 radians can pass through the retarding grid. In terms of mass number this corresponds to ions of 27 and 15 AMU

when the resonant ion is 20 AMU. The accepted ions since they have not lost all of their kinetic energy are intercepted by the ion current collector. This ion current signal produces the lines of the mass spectrum.

For stability purposes the potential V_R is derived from the V_{RF} source. Hence, incremental changes in V_{RF} will change V_R a proportional amount and the V_R/V_{RF} ratio will remain constant, the condition for stability.

Multicharged Ions

Analysis of multicharged ions, ηe , by RF velocity selection is identical to that of the singly charged ion except that the apparent mass of the ion is M/η . The fact that the energy gained by multicharged ions is η times greater than that of a singly charged ion has been suggested as a means of separating ions of multiplicity η , the assumption being that since the energy gain is η times greater the multicharged ion can readily pass through the retarding potential field set to $V_{R(max)}$ for singly charged ions. The assumption is incorrect. The retarding potential V_R exerts a force ηV_R on all ions. Thus an ion of charge η which gains η times the energy is retarded by a force ηV_R times as large as that of a singly charged ion and hence cannot be distinguished on the basis of charge.

Multistage Spectrometers

As mentioned previously, the mass resolution of a single stage is insufficient for most spectrometer applications. However, mass resolution can be increased by increasing the number of times energy is imparted to the ion. This is done in multistage spectrometers which consist of two or more RF analyzer stages separated by equipotential drift spaces. In order to impart the maximum energy to an ion in each stage the center to center grid spacings are made equal to the distance the selected ion travels in an in-

tegral number of RF cycles. Judicious selection of the number of cycles between stages and the order in which they occur, for three or more stages, will optimize both mass resolution and available retarding potential range without the introduction of spurious peaks in the spectra.

Multistage spectrometers are identified by the number of stages and the number and order of RF cycles between successive stages, for example 3-stage 7-5 cycle or 4-stage 13-11-7 cycle. Figures 3 and 4 show pictorially and schematically a 3-stage 7-5 cycle spectrometer, without an ion source, with appropriate electronics in block form for positive ion analysis.

Multistage Energy Gain

A simplified equation for a multistage spectrometer can be obtained by integrating the energy gain equation for each stage with appropriate limits of integration. As with the single stage it is assumed that the ion velocity is constant in the analyzer section. For a 3-stage spectrometer the energy gain equation is

$$\begin{aligned} \Delta w = vE_0 & \left(\int_{-s/v}^0 \sin(\omega t + \theta) dt \right. \\ & + \int_0^{s/v} -\sin(\omega t + \theta) dt \\ & + \int_{\beta_1 s/v - s/v}^{\beta_1 s/v} \sin(\omega t + \theta) dt \\ & + \int_{\beta_1 s/v}^{\beta_1 s/v + s/v} -\sin(\omega t + \theta) dt \\ & + \int_{(\beta_1 + \beta_2)s/v - s/v}^{[(\beta_1 + \beta_2)s]/v} \sin(\omega t + \theta) dt \\ & + \int_{(\beta_1 + \beta_2)s/v}^{[(\beta_1 + \beta_2)s]/v + s/v} \\ & \left. - \sin(\omega t + \theta) dt \right) \text{ ergs} \end{aligned} \quad (6)$$

where the drift time between center grids in terms of n , the number of resonant RF

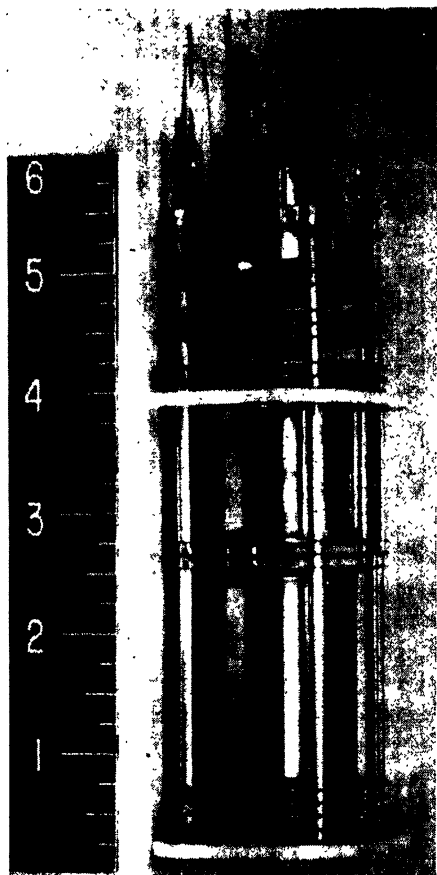


Fig. 3. Three-stage 7-5 cycle Bennett RF mass spectrometer without ion source designed for use within a metal envelope. The grid arrangement is identical to that given in Fig. 4. Grids are mounted on four ceramic coated tungsten rods of which two are clearly visible. Distance between grids is fixed by glass spacers which fit over the rods. Spacers are matched so that all grids are parallel. The metal cylinders which form the 7 and 5 cycle equipotential drift spaces do not act as spacers. The white units at the front and four inch positions are "Teflon" plastic spacers to position the spectrometer within its envelope.

cycles between stages, is

$$nt = n \left(\frac{v}{2\pi f} \right) \frac{2\pi}{v} = \frac{2.695ns}{v} = \frac{\beta s}{v} \quad (7)$$

$$\beta_1 = 2.695n_1, \quad \beta_2 = 2.695n_2, \text{ etc.}$$

Integrating and simplifying Equation (6)

gives the following expression for a 3-stage analyzer.

$$V(\alpha\theta) = \frac{\Delta w}{e} = -2\sqrt{2}V_{RF_{rms}} \left(\frac{1 - \cos \alpha}{\alpha} \right) \cdot (\cos \theta + \cos(\alpha\beta_1 + \theta) + \cos(\alpha(\beta_1 + \beta_2) + \theta)) \text{ volts} \quad (8)$$

With respect to variations in θ the energy gain in Equation (8) is identical to that of a single stage and consequently has its first and principal maximum at π radians. With respect to variations in α Equation (8) has a series of maxima due to the multistage function

$$[1 + \cos \alpha\beta_1 + \cos \alpha(\beta_1 + \beta_2)]_{\theta=\pi} \quad (8a)$$

which rapidly modulates the single-stage energy function,

$$2\sqrt{2}V_{RF} \left(\frac{1 - \cos \alpha}{\alpha} \right). \quad (8b)$$

Equation (8) has its principal maximum at $\alpha_0 = 2.3311$, regardless of the integer values of n_1 and n_2 associated with β_1 and β_2 . Ions satisfying this condition produce the fundamental peaks of the mass spectra. Equation (5) gives the mass of these fundamental peaks. Secondary maxima occur at values dependent on the values of β_1 and β_2 . The solid curve of Figure 5 shows these peaks, for $\theta = \pi$, in the neighborhood of α_0 for a 7-5 cycle analyzer; ($\beta_1 = 2.695 \times 7$, $\beta_1 + \beta_2 = 2.695(7 + 5)$); their amplitudes are always less than the principal or fundamental peak amplitude. These secondary peaks are called harmonics and are readily distinguished from the fundamental on the basis of maximum energy gained. Frequently the introduction of harmonic peaks into the mass spectra is thought to be undesirable. Consequently they are avoided by adjusting V_x above the harmonic level. An important point to note about multistage tubes is that an ion of mass M gains energy at discrete but related values of α as opposed to the broad distribution of a single stage.

BENNETT RADIO FREQUENCY SPECTROMETER

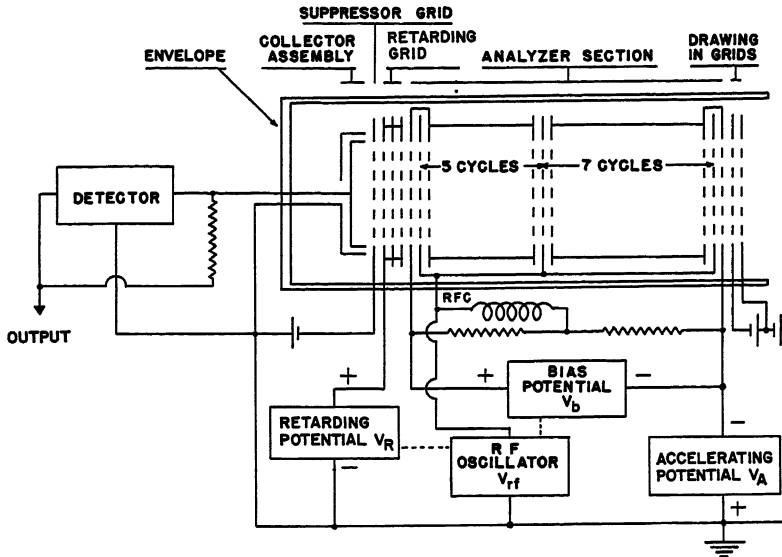


FIG. 4. Block diagram of three-stage 7-5 cycle spectrometer and electronics for analysis of positive ions. For negative ion analysis, the potential on each grid is reversed. The DC bias potential V_b , not discussed in the text, is required when the energy gain per stage is appreciable compared to the energy acquired by the ion from V_A . The bias, V_b , is adjusted to a value of $(2.05) (V_{RF})$ volts per stage across which it appears. In a three-stage tube the bias is applied across the middle stage with a polarity that retards the resonant ion by an amount equal to that which it gains from V_{RF} in that stage. Hence the bias potential assures that the resonant ion has the same velocity in the second drift space as in the first. Dotted lines between V_{RF} , V_R and V_b indicate that they are derived from the same source, generally V_{RF} , to insure stable operation independent of power supply variations.

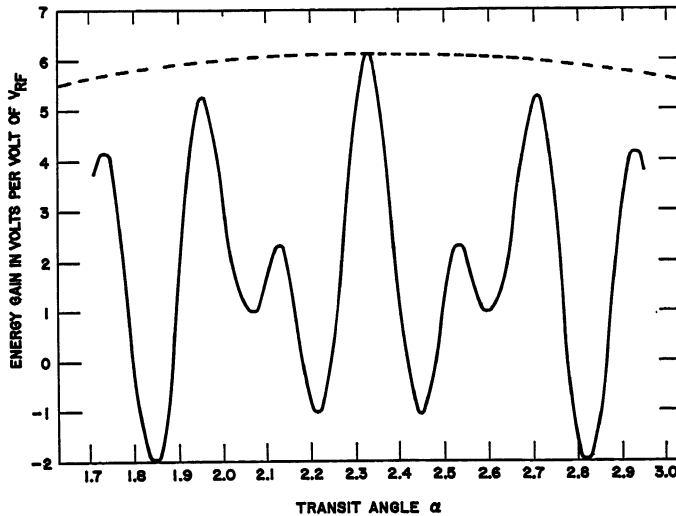


FIG. 5. Energy gain for three-stage 7-5 cycle spectrometer for $\theta = \pi$ radians in the neighborhood of $\alpha_0 = 2.3311$. Dotted curve is the energy gain of a single stage times three.

The reason for the increase in mass resolution is now apparent if one compares the solid curve to the dotted one, ($3\times$ single gain stage) and notes how the energy gain varies for small changes in α . For example consider the ion which has a transit angle of $\alpha_0 \pm \Delta\alpha$ and satisfies the condition $\theta = \pi$. Then in the first stage it will gain for all practical purposes maximum energy. But in traversing the drift space between stages the factor, $\Delta\alpha$, is multiplied by the number of cycles n_1 and $n_1 + n_2$, causing the ion to fall out of resonance with the RF and cross the center grid of successive stages at other than the optimum phase angle with a corresponding decrease in energy gain. It is this multiplication of the transit angle increment $\Delta\alpha$ as the ion traverses the drift spaces that is responsible for improved mass resolution.

Resolving Power and Current Efficiency

Resolving power is defined as $M_0/\Delta m$, where M_0 is the mass of the resonant ion and Δm is the mass difference between the resonant ion and the ions which are just rejected by V_R . Theoretical current efficiency for the resonant ion is defined as the ratio

current collected/current entering the spectrometer

$$I_c/I_0 = 2(\theta - \theta_0)/2\pi$$

where $2(\theta - \theta_0)$ is the RF phase angle during which ions receive sufficient energy in the analyzer to pass through the retarding potential grid. Expressions for both of these quantities are derived from a Taylor series expansion of the energy gain equation, see appendix, and give for a spectrometer of N stages

$$\frac{M}{\Delta m} = 1.1 \sqrt{\frac{n_1^2 + (n_1 + n_2)^2 \cdots (n_1 \cdots n_{N-1})^2}{N \left[1 - \frac{V_R}{V_{R\max}} \right]}} \quad (9)$$

and

$$\left(\frac{\theta - \theta_0}{\pi} \right)_{\text{theo}} = \frac{\sqrt{2}}{\pi} \sqrt{1 - \frac{V_R}{V_{R\max}}} \quad (10)$$

Thus the resolving power is dependent on four factors: (1) the total number of cycles in the spectrometer, (2) the order in which the cycles are arranged, (3) the number of stages, and (4) the fractional level at which the retarding potential is set. Theoretical current efficiency (Figure 6), on the other hand, is dependent only on the fractional

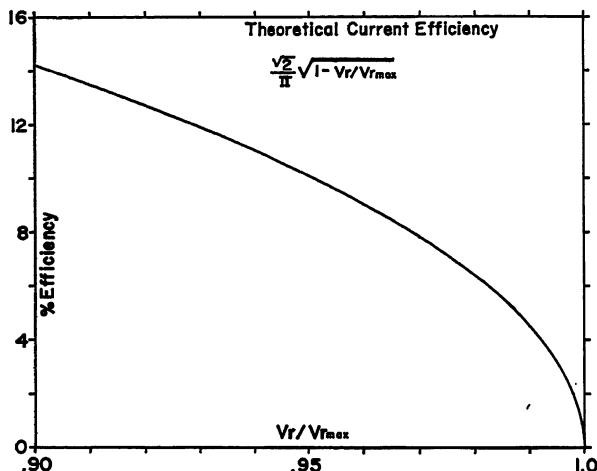


FIG. 6. Theoretical current efficiency for a Bennett radio frequency mass spectrometer. V_R is the retarding potential and $V_{R\max} = \frac{\Delta w}{e}$ is the maximum energy gain, in volts, of the resonant ion as it leaves the analyzer.

level of the retarding potential and is the same for all spectrometers. A more realistic efficiency value takes into account the physical transmission efficiency of at least the grids in the analyzer section. If ξ is the per cent transparency of a grid to ions, then Equation (10) becomes

$$\left(\frac{\theta - \theta_0}{\pi}\right) = \sqrt{2} \frac{\xi^N}{\pi} \sqrt{1 - \frac{V_R}{V_{Rmax}}}. \quad (11)$$

Practical values of ξ for a wire mesh grid are about 90–95 %, based on optical transparency measurements. (The optical transmission of 9 grids, measured in the visible, was $\xi^9 = 0.5$ or $\xi = 92.6$ %.)

Design Considerations

The product of resolving power and current efficiency provides a convenient performance index, P , for the Bennett RF spectrometer

$$P = \frac{0.5\xi^N}{\sqrt{N}} \quad (12)$$

$$\cdot \sqrt{n_1^2 + (n_1 + n_2)^2 + \cdots + (n_1 \cdots n_{N-1})^2}$$

from which two pertinent facts can be deduced. First, for a given tube, P is independent of retarding potential. This permits mass resolution and current efficiency to be interchanged, one at the expense of the other. Second, since N appears in Equation (12) in both the exponent of ξ and in the denominator, increasing the number of stages of a wire grid spectrometer while keeping the same number of cycles in the tube does not increase P . Table 1 lists the values of

$$\frac{0.5\xi^N}{\sqrt{N}}$$

for $\xi = 92.6$ %, showing that the two stage spectrometer has the largest P value for a given number of cycles. One should be cautious about using a two-stage tube without considering the position and level of the harmonic peaks. For example, a two-stage,

TABLE 1

N	$\frac{0.5 \xi^N}{\sqrt{N}}$ for $\xi = 92.6$
2	0.221
3	0.143
4	0.098
5	0.069

12-cycle spectrometer has a P value of 2.63, with harmonic peaks 99.2 % of the fundamental at $\alpha = 2.524$ and 2.14. If the tube is converted to a three-stage 7–5 cycle unit (12 total) the P value is 1.98, with the largest harmonic peaks 85 % of the fundamental at $\alpha = 2.715$ and 1.952. The reason for introducing additional stages is evident; they reduce the amplitude of harmonic peaks but at the expense of P . The optimum position of the middle stage or stages to reduce harmonics depends on the total number of cycles in the tube and may be obtained by graphically solving the energy equation of the tube, or in simpler form its modulation function; i.e., Equation (8) or (8a), respectively, for a three-stage tube. The solid curve of Figure (5) was constructed using the graphical method. The dotted curve is the single stage energy function.

Energetic Ions and Mass Identification by Harmonics

The mass of the resonant ion detected by the Bennett spectrometer is given in terms of the potential, in volts, through which the ion has fallen upon entering the analyzer. Generally this potential is entirely the accelerating voltage applied between the ion source and the analyzer. The resonant mass is then directly determined from Equation (5). In case the entering ion has acquired an initial but undetermined energy K (in volts) from some source external to the spectrometer system the total potential in volts, $V = V_A + K$, contains the unknown quantity K resulting in an ambiguous determina-

tion of M . This problem can be solved if harmonics are allowed to appear in the spectra.

As was shown earlier, a harmonic peak is produced by ions of mass M which pass through the analyzer at a value of α other than α_0 for the resonant ion. Consequently, for a voltage swept spectrometer, two equations for the mass M ion can be written,

$$M = \frac{0.286(V_A + K)}{s^2 f^2} \quad (13)$$

for the fundamental peak, and

$$M = \frac{0.286(V_{A_h} + K)(1 \pm h_a)}{s^2 f^2} \quad (14)$$

for the harmonic peaks. V_A and V_{A_h} are the respective accelerating potentials at which the fundamental and harmonic peaks occur. The term

$$\frac{\alpha}{\alpha_0} = (1 \pm h_a) \quad (15)$$

is defined as the harmonic ratio; a is an integer and the value of h_a depends on the number of cycles in the tube and their arrangement. Values for Equation (15) are readily obtained from a plot of the energy gain equation. Peaks associated with minus values of h_a are called upper harmonics, those with plus values are the lower harmonics. The nomenclature originates from the position of the harmonics on the mass scale relative to the fundamental ($h_a = 0$). Eliminating K , the unknown energy, between Equations (13) and (14) gives the mass of the singly charged ion

$$M = \frac{0.286}{s^2 f^2} \frac{(V_A - V_{A_h})}{1 - \left(\frac{1}{1 \pm h_a}\right)^2} \quad (16)$$

$$= \frac{\Delta M}{1 - \left(\frac{1}{1 \pm h_a}\right)^2}$$

as a function of the physical parameters of the spectrometer but independent of the

initial energy. The Bennett spectrometer is an absolute instrument when operated in this manner.

When two fundamental peaks, due to energetic ions, and their respective harmonic peaks are present in the same spectrum the following relationship exists for the mass of the lighter ion M_x in terms of the mass difference ΔM_{xy} between M_x and the heavier mass M_y , and the apparent mass difference between the fundamentals and their respective harmonics ΔM_x and ΔM_y .

$$M_y = \frac{\Delta M_{xy} \cdot \Delta M_y}{\Delta M_y - \Delta M_x} \quad (17)$$

This method of mass identification is appealing since it depends on mass differences which are readily obtained from the voltages of the peaks concerned and the proportionality constant of the spectrometer.

Appendix

Mass Resolution and Current Efficiency. Mass resolution for the Bennett RF mass spectrometer is defined as

$$\frac{M_0}{\Delta m} = \frac{M_0}{2(M - M_0)} \quad (a)$$

where M_0 is the resonant mass and M is the adjacent higher mass which is just rejected by the retarding potential when the spectrometer is adjusted to M_0 . Physically this is interpreted to mean that the skirt of the M mass peak contributes nothing to the center of the M_0 peak. Rewriting (a) in terms of the transit angle

$$\alpha = \frac{sv}{v} = \frac{sv}{\sqrt{\frac{2ev}{m_0}}} \sqrt{M}$$

one has

$$\frac{M_0}{\Delta m} = \frac{(\alpha_0^2)}{2(\alpha^2 - \alpha_0^2)} \quad (b)$$

By inspection of Figure (2) one notes that for a spectrometer adjusted to the resonant mass, $\alpha_0 = 2.3311$, ions gain sufficient energy

to pass through the retarding grid and reach the collector only during a small portion of an RF cycle $\Delta\theta$. Theoretical current efficiency $I_c/I_{0\text{thso}}$ is the ratio of the resonant ion current I_c reaching the collector during $\Delta\theta$ to the total resonant ion current entering the spectrometer, or expressed in terms of phase angles

$$I_c/I_{0\text{thso}} = \frac{\Delta\theta}{2\pi} \frac{\theta - \theta_0}{\pi} \quad (c)$$

where θ is the phase angle at which current ceases to flow and θ_0 is the phase angle at which maximum current flows ($\theta_0 = \pi$).

Before deriving the equations for mass resolution and current efficiency one should recognize that they are independent of each other since they are functions of the orthogonal parameters α and θ but that both are dependent on the retarding potential level V_R .

Equations for mass resolution and current efficiency are derived from the following three term Taylor series expansion about $\alpha_0 = 2.3311$ and $\theta_0 = \pi$:

$$\begin{aligned} V(\alpha\theta) &= V(\alpha_0\theta_0) + \{hV_\alpha(\alpha_0\theta_0) + kV_\theta(\alpha_0\theta_0)\} \\ &+ \frac{1}{2} \{h^2V_{\alpha\alpha}(\alpha_0\theta_0) + 2hkV_{\alpha\theta}(\alpha_0\theta_0) \\ &+ k^2V_{\theta\theta}(\alpha_0\theta_0)\} \end{aligned} \quad (d)$$

of the multistage energy gain equation

$$\begin{aligned} V(\alpha\theta) &= \frac{\Delta w}{e} = -2\sqrt{2} V_{RF} \left(\frac{1 - \cos \alpha}{\alpha} \right) \\ &\cdot [\cos \theta + \cos(\alpha\beta_1 + \theta) \\ &+ \cos(\alpha(\beta_1 + \beta_2) + \theta) \\ &\dots \cos(\alpha(\beta_1 + \beta_{N-1}) + \theta)]. \end{aligned} \quad (e)$$

Only three terms are used in equation (d) as it is assumed that contributions from higher order terms are negligible for small values of h and k . In order that quantities in equation (d) will be compatible with the form required by equations (b) and (c) let

$$h = \theta - \theta_0$$

and

$$h \simeq \frac{(h + \alpha_0)^2 - \alpha_0^2}{2\alpha_0} = \frac{\alpha^2 - \alpha_0^2}{2\alpha_0}.$$

By definition both first derivatives, $V_\alpha(\alpha_0, \theta_0)$ and $V_\theta(\alpha_0, \theta_0) = 0$; hence, the Taylor series expansion simplifies to

$$\begin{aligned} 2[V(\alpha\theta) - V(\alpha_0\theta_0)] &= \left[\left(\frac{\alpha^2 - \alpha_0^2}{2\alpha_0} \right)^2 V_{\alpha\alpha}(\alpha_0\theta_0) \right. \\ &+ 2 \left(\frac{\alpha^2 - \alpha_0^2}{2\alpha_0} \right) (\theta - \theta_0) V_{\alpha\theta}(\alpha_0\theta_0) \\ &\left. + (\theta - \theta_0)^2 V_{\theta\theta}(\alpha_0\theta_0) \right]. \end{aligned} \quad (f)$$

Differentiating and evaluating equation (e), with the simplifying assumption that

$$-2\sqrt{2} V_{RF} \left[\frac{1 - \cos \alpha}{\alpha} \right] = Y$$

is constant over the interval h , one has

$$\begin{aligned} V(\alpha_0\theta_0) &= YN \\ V_{\alpha\alpha}(\alpha_0\theta_0) &= -Y(\beta_1^2 + (\beta_1 + \beta_2)^2 + \dots \\ &+ (\beta_1 + \dots + \beta_{N-1})^2) \\ V_{\theta\theta}(\alpha_0\theta_0) &= -YN \\ V_{\alpha\theta}(\alpha_0\theta_0) &= -Y(\beta_1 + (\beta_1 + \beta_2) + \dots \\ &+ (\beta_1 + \dots + \beta_{N-1})) \end{aligned}$$

Substituting these values in equation (f) and simplifying gives

$$\begin{aligned} 2N \left[1 - \frac{V(\alpha\theta)}{V(\alpha_0\theta_0)} \right] &= \left(\frac{\alpha^2 - \alpha_0^2}{2\alpha_0} \right)^2 \\ &\cdot (\beta_1^2 + (\beta_1 + \beta_2)^2 + \dots + (\beta_1 + \dots + \beta_{N-1})^2) \\ &+ 2 \left(\frac{\alpha^2 - \alpha_0^2}{2\alpha_0} \right) (\beta_1 + (\beta_1 + \beta_2) + \dots \\ &+ (\beta_1 + \dots + \beta_{N-1})(\theta - \theta_0) + N(\theta - \theta_0)^2). \end{aligned}$$

from which one can solve for current efficiency

$$\frac{I_c}{I_{0\text{thso}}} = \frac{\theta - \theta_0}{\pi\alpha - \alpha_0} = \frac{\sqrt{2}}{\pi} \left(1 - \frac{V_R}{V_{R\text{max}}} \right)^{1/2}$$

and mass resolution

$$\frac{M_0}{\Delta m} = \frac{\alpha_0^2}{2(\alpha^2 - \alpha_0^2)_{\theta=\theta_0}}$$

$$= 1.1 \left(\frac{n_1^2 + (n_1 + n_2)^2 + \dots + (n_1 + \dots + n_{N-1})^2}{N \left(1 - \frac{V_R}{V_{R_{\max}}} \right)} \right)^{1/2}$$

REFERENCES

Theory

1. BENNETT, W. H., "Radiofrequency Mass Spectrometer," *J. Applied Phys.*, **21**, 143-149 (1950).
2. U. S. Patent 2,535,032
3. U. S. Patent 2,721,271
4. WHEERRY, T. C. AND KARASEK, F. W., "Performance of the Nonmagnetic Radiofrequency Mass Spectrometer Tube," *J. Applied Phys.*, **26**, 682-685, (1955).
5. CANNON, W. W. AND TESTERMAN, M. K., "Accurate Mathematical Treatment of the Analyzer of the RF Mass Spectrometer Tube," *J. Applied Phys.*, **27**, 1283-1286 (1956).
6. JOHNSON, C. Y., "Mass Determination of Ions Detected by Bennett Ion RF Mass Spectrometer," *J. Applied Phys.*, **29**, 740-741 and 1134 (1958).

Note: In deriving the theory of the RF analyzer various authors reference time to the first grid instead of the center grid of the first stage as was done in this article. The resultant equations, although equivalent, are more complicated.

Application

7. TOWNSEND, J. W., JR., "Radiofrequency Mass Spectrometer for Upper Air Research," *Rev. Sci. Instr.*, **23**, 538-541 (1952).
8. TOWNSEND, J. W., JR., MEADOWS, E. B., AND PRESSLY, E. C., "A Mass Spectrometric Study of the Upper Atmosphere" in *Rocket Exploration of the Upper Atmosphere*, Edited by R. L. F. Boyd and M. J. Seaton, Pergamon Press Ltd., London (1954).
9. JOHNSON, C. Y., AND MEADOWS, E. B., "First Investigation of Ambient Positive-Ion Composition to 219 Km by Rocket-Borne Spectrometers," *J. Geophysical Res.*, **60**, 193-203 (1955).
10. MEADOWS, E. B. AND TOWNSEND, J. W., JR., "Diffusive Separation in the Winter Night-

time Arctic Upper Atmosphere 112 to 150 Km," *Ann. Geophysique*, **14**, 80-93 (1958).

11. TOWNSEND, J. W., JR. AND MEADOWS, E. B., "Density of the Winter Nighttime Arctic Upper Atmosphere 110 to 170 Km," *Ann. Geophysique*, **14**, 117-130 (1958).
12. JOHNSON, C. Y., MEADOWS, E. B. AND HOLMES, J. C., "Ion Composition of the Arctic Ionosphere," *J. Geophysical Res.*, **63**, 443 (1958).
13. TOWNSEND, J. W., JR., JOHNSON, C. Y., HOLMES, J. C., AND MEADOWS, E. B., "Atmospheric Composition at Arctic High Altitudes," In *Experimental Results of U. S. IGY Rocket Program to 1 July 1958*, IGY Rocket Report Number 1, National Academy of Sciences, National Research Council, Washington 25, D. C. (1958). (Reprints of References 10, 12 and 15 also appear in this volume.)
14. HOLMES, J. C., AND JOHNSON, C. Y., "Probing the Upper Atmosphere," *Anal. Chem.*, **30**, 19A-26A (1958).
15. JOHNSON, C. Y., HEPPNER, J. P., HOLMES, J. C., AND MEADOWS, E. B., "Results Obtained with Rocket-Borne Ion Spectrometers," *Ann. Geophysique*, **14**, 475-482 (1958).
16. HOLMES, J. C., AND JOHNSON, C. Y., "Positive Ions in the Ionosphere," *Astronautics*, **4**, No. 30-31 (1958).

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COMPLEX MIXTURES OF ALCOHOLS AND WATER: THE FISCHER-TROPSCH PRODUCT*

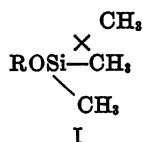
Direct mass spectrometric determination of alcohols above C_3 in the presence of hydrocarbons is not possible because of a similarity in fragmentation patterns.⁵ Analysis of mixtures of alcohols and hydrocarbons is of special interest, because they are the chief product of the Fischer-Tropsch synthesis.^{1-4, 9, 11, 14} With nitrated iron catalysts, primary straight-chain alcohols may constitute the major portion of the product.^{2, 11}

Work on the Fischer-Tropsch and similar processes has been hampered by the lack of suitable procedures for determining alcohols. Herein is described a new approach for the rapid and accurate determination of alcohols

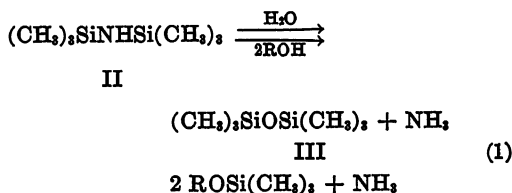
* Based on paper in *Analytical Chemistry*, **30**, 1353 (1958), by permission.

in the presence of paraffins, olefins, and other hydrocarbons without the lengthy and relatively complex distillations previously applied to Fischer-Tropsch products.^{2, 4, 9-14}

This method is based on the quantitative conversion of alcohols to their trimethylsilyl derivatives, trimethylsilyl ethers (I).^{7, 10, 13} The major mass spectral peaks suitable for analysis no longer correspond to those obtained from hydrocarbons. Carbon-silicon bonds in trimethylsilyl ethers are split in the mass spectrometer to give intense parent (molecule ion) minus 15 peaks, which result from the loss of a methyl group.¹³



Hexamethyldisilazane (II) is used as a converting reagent and reacts with alcohols and water to give trimethylsilyl ethers and hexamethyldisiloxane (III), respectively, as shown in Equation 1.⁷ Both reactions evolve ammonia. The mixture treated with hexamethyldisilazane is analyzed directly in the mass spectrometer.



Discussion

Mass Spectra. Data for a large number of trimethylsilyl derivatives have been presented in detail and discussed.¹² Analysis of alcohols as trimethylsilyl ethers extends the usable range of the conventional, room temperature mass spectrometer. Ordinarily, usable mass spectra for C₁₀ and C₁₁ alcohols cannot be obtained in the room temperature instrument because of limited volatility and/or sorption in the system.

The substitution of the trimethylsiloxy

group for the alcoholic hydroxyl group causes a shift of important mass spectral peaks into higher mass ranges where interferences are less likely to occur. It is the inclusion of both oxygen and silicon in the ion fragments which leads to the distinctive mass spectral peaks 4 mass units above the principal ones obtained from alkanes. Oxygen, mass 16, is equivalent to a methylene group plus 2 mass units. Silicon, mass 28, is equivalent to two methylene groups; its valence of 4 means that two additional alkyl groups can be held when it is included in a hydrocarbon chain. This results in an additional shift of 2 mass units.

Synthetic Alcohol Mixtures. To utilize trimethylsilyl ethers to determine alcohols, it is necessary to use a reagent that quantitatively converts the alcohols to their trimethylsilyl derivatives. The choice of hexamethyldisilazane as a converting reagent was based on experience with this reagent in preparing trimethylsilyl ether standards⁷; the losses were from routine handling and slight hydrolysis of the trimethylsilyl ethers, when they were not carefully protected from atmospheric moisture. The strong 146 mass spectral peak for hexamethyldisilazane allows determination of excess reagent and thereby a correction for contributions of the reagent to lower mass peaks.

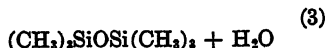
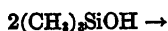
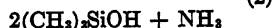
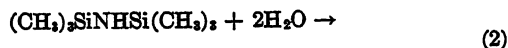
A number of hydrocarbon-alcohol mixtures were prepared and analyzed by mass spectrometry after treatment with hexamethyldisilazane. Successful determination of the hydrocarbons and alcohols as trimethylsilyl ethers indicates quantitative conversion of the alcohols to trimethylsilyl ethers. Results obtained from the trimethylsilyl ether analysis are reported in terms of the original alcohol composition by using standard molecular conversion factors, known alcohol densities, and the trimethylsilyl ether densities previously reported.⁷ Blending of mixtures of trimethylsilyl ethers in the mass spectrometer system with oxygenate-hydrocarbon mixtures from the Fischer-Tropsch process showed no inter-

ference from hydrocarbon ion fragmentation peaks; thus, trimethylsilyl ethers could be determined in the presence of these added hydrocarbons and oxygenates.

Water. As water reacts with hexamethyldisilazane to form hexamethyldisiloxane (Equation 1), it does not interfere with the conversion of the alcohols to their trimethylsilyl ethers. Sufficient hexamethyldisilazane must be used to react with the water, which has a relatively low equivalent weight.

Because of the distinctive 147 mass spectral peak¹² hexamethyldisiloxane can be used for determination of water.

The reaction between hexamethyldisilazane and water is more complicated than indicated by Equation 1. However, it can be discussed in terms of Equations 3 and 4, where trimethylsilanol (IV) is an intermediate.



The water from Equation 3 can react with more hexamethyldisilazane, so that it is eventually converted to hexamethyldisiloxane and ammonia. When water is initially present at concentrations approaching 25%, a considerable amount of hexamethyldisiloxane is formed. Then, trimethylsilanol appears moderately stable, and longer periods of re-

flux are necessary for complete reaction. The condensation reaction is complex, but both the mechanism and kinetics have been studied under special conditions by Grubb.⁶

Reaction probably could be speeded by generating greater concentrations of hydrochloric acid, using more trimethylchlorosilane initially. However, the water determination need not be deferred until complete condensation of trimethylsilanol. An alcohol-water mixture can be analyzed by taking into account the contributions of the trimethylsilyl ethers and hexamethyldisiloxane to the mass 75 peak and considering the residual portion of this peak to result from trimethylsilanol.

Fischer-Tropsch Products. Three applications of the trimethylsilyl ether conversion technique are illustrated in Tables 1 and 2. The determination of total alcohols and alcohol distribution from C₂ to C₈ in a raw synthetic gasoline fraction known to contain predominantly primary straight-chain alcohols is shown in Table I. Infrared functional group analysis was in excellent agreement with total alcohol content determined by mass spectrometry.

Data on alcohol distribution in several cuts from the distillation of a Fischer-Tropsch product are shown in Table I. Alcohol distribution is as expected if the complexity of the Fischer-Tropsch product and the many possibilities for azeotrope formation are considered. It is difficult to decide

TABLE 1. MASS SPECTRAL DETERMINATION OF ALCOHOLS IN FISCHER-TROPSCH PRODUCTS

Fraction	Alcohols as Trimethylsilyl Ethers, Vol. %								Total Alcohol, Vol. %	
	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	M. S.	I. R.
Raw gasoline, 0-200° C.	1.5	5.4	3.8	2.8	1.0	0.5	0.4		15.4	14.9 ^a
0-100° C. cut		Tr.	2.4	4.0					6.4	6.6 ^b
100-150° C. cut		2.8	30.2	34.2	11.6	0.3			79.1	70.3 ^b
150-200° C. cut				0.4	4.3	5.0	2.7	0.4	12.8	15.8 ^b

^a Approximation from functional group determination; based on molecular weight of 70.

^b Approximation from functional group determination; average molecular weight estimated from mass spectrometer data.

on an average molecular weight for the alcohols in a cut without prior knowledge of alcohol distribution. Without these data, total alcohol by infrared analysis can only be estimated. Using these data, the infrared and mass spectrometric determinations of Table 1 are in good agreement except for the 100° to 150° C. cut.

Analysis of a product-water phase obtained from a Fischer-Tropsch liquid product is shown in Table 2. Methyl, ethyl, and propyl alcohol give unique mass spectral peaks, but interfering fragmentation from hydrocarbons and oxygenated compounds allows only limits to be placed on the concentrations of higher alcohols and other oxygenates. Using the trimethylsilyl ethers, the volume per cent unknown is reduced from 22.2 to 9.3 %. Ethanol is used as an internal standard to combine data on the higher alcohols obtained from the trimethylsilyl derivatives with data on other components from the direct, mass spectrometric analysis. Constancy of the ethanol-propanol ratio in the two analyses is evidence for the validity of this procedure. Determinations from trimethylsilyl ether derivatives fall within the limits set by direct analysis. Data from Tables 1 and 2 illustrate the detection of alcohol concentrations of less than 1 %.

Branching. When mixtures containing large amounts of branched and secondary alcohols are to be analyzed, alcohol determination becomes more complex.^{5, 15} It would be necessary to fractionate the samples into relatively narrow cuts to use the trimethylsilyl ethers as a basis for mass spectrometric analysis. For example, a C₆ cut might be distilled to contain only C₅ and C₆ or C₆ and C₇ alcohols. Branched components in a Fischer-Tropsch product could be 2- and 3-methylpentanol.

Matrices based on the following observations might serve as a basis for determining alcohols in the presence of hydrocarbons. Parent minus 15 peaks for the normal trimethylsilyl ethers are 145, 159, and 173. In-

TABLE 2. ANALYSIS OF AQUEOUS SOLUTION OF ALCOHOLS

	Volume %	
	As alcohol	As trimethylsilyl ether
H ₂ O	24.1	(24.1) ^{a, b}
Alcohols		
C ₁	4.4	(4.4)
C ₂	28.8	28.8 ^c
C ₃	15.1	15.7
C ₄	13.7 max. 5.4 min.	9.2
C ₅	8.4 max.	5.9
C ₆	7.2 max.	2.0
C ₇		0.5
C ₈		0.1
Acetone	3.3 max.	(3.3 max.)
Methyl ethyl ketone	1.2 max.	(1.2 max.)
Unknown	22.2 ^d	4.8-9.3

^a H₂O based on (CH₃)₃Si₂O is 23.5%.

^b Parentheses indicate data retained from direct analysis.

^c Internal standard.

^d Unknown based on minimum C₄ value, maximum value not included.

tensities for the methyl-branched ethers are lower than the intensities for the normal ethers. Mass 103 for the 2-methylpentyl trimethylsilyl ether is more intense than for other components of the mixture under consideration. Mass 89 shows increased intensity for the 3-methylpentyl trimethylsilyl ether. Ratio of 73 to 75 intensity is different for normal and branched-chain alcohol derivatives.¹² Probably, the presence of secondary alcohols in narrow boiling fractions can be determined from cleavage at the functional carbon atom.¹² Also, identification of secondary alcohols might be possible from direct, mass spectrometry.⁵

Other Applications

The lower methyl ketones, especially acetone, undergo a variety of acid- and base-catalyzed condensation and addition reactions under the conditions of conversion of alcohols to trimethylsilyl ethers. Caution

must be exercised in applying the technique described to solutions containing large concentrations of these ketones. Because trimethylsilyl derivatives give characteristic peaks in the mass spectrometer, a number of other applications are suggested.

The mass spectra of the trimethylsilyl derivatives of phenol and resorcinol have been obtained.¹² An analytical mass spectral procedure utilizing the trimethylsilyl derivatives of the phenols may be practical. Glycol mixtures may also be amenable to analysis as trimethylsilyl derivatives.¹²

As primary amines react with hexamethyldisilazane to give trimethylsilyl derivatives⁷ with intense parent minus 15 peaks,⁸ these derivatives could be a basis for the determination of primary amines. The trimethylsilyl derivatives of mercaptans also give intense parent minus 15 peaks.¹² The problem is conversion, because hexamethyldisilazane does not react readily with mercaptans.⁷

Hexamethyldisilazane is an interesting possibility as a reagent for the analysis of heavy water for deuterium and oxygen-18. Ammonia formed in the course of reaction between the hexamethyldisilazane and water could be analyzed by mass spectrometry to determine deuterium. The hexamethyldisiloxane formed could be used for the oxygen-18 determination.

REFERENCES

1. ANDERSON, R. B., *Advances in Catalysis* **5**, 355 (1953).
2. ANDERSON, R. B., FELDMAN, J., STORCH, H. H., *Ind. Eng. Chem.*, **44**, 2418 (1952).
3. ANDERSON, R. B., SHULTZ, J. F., U. S. PATENT 2,629,728 (Feb. 24, 1953).
4. CAIN, D. G., WEITKAMP, A. W., BOWMAN, N. J., *Ind. Eng. Chem.* **45**, 359 (1953).
5. FRIEDEL, R. A., SHULTZ, J. L., SHARKEY, A. G., JR., *Anal. Chem.* **28**, 926 (1956).
6. GRUBB, W. T., *J. Am. Chem. Soc.*, **76**, 3408 (1954).
7. LANGER, S. H., CONNELL, S., WENDER, I., *J. Org. Chem.*, **23**, 50 (1958).
8. LANGER, S. H., FRIEDEL, R. A., WENDER, IRVING, SHARKEY, A. G., JR., unpublished results.
9. MORRELL, C. E., CARLSON, C. S., MCATEER, J. H., ROBEY, R. S., SMITH, P. V., JR., *Ind. Eng. Chem.* **44**, 2839 (1952).
10. SAUER, R. O., *J. Am. Chem. Soc.* **66**, 1707 (1944).
11. SCHLESINGER, M. D., BENSON, H. E., MURPHY, E. M., STORCH, H. H., *Ind. Eng. Chem.* **46**, 1322 (1954).
12. SHARKEY, A. G., JR., FRIEDEL, R. A., LANGER, S. H., *Anal. Chem.* **29**, 770 (1957).
13. SPRUNG, M. M., NELSON, L. S., *J. Org. Chem.* **20**, 1750 (1955).
14. STEITZ, ALFRED, JR., BARNES, D. K., *Ind. Eng. Chem.* **45**, 353 (1953).
15. YARBOROUGH, V. A., *Anal. Chem.* **25**, 1914 (1953).

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DIFFUSION COEFFICIENTS,
MEASUREMENT OF

In the normal operation of the mass spectrometer, the instrument is used to measure the amount of a particular gas in a fixed gas sample. There are many experiments however, in which it is desirable to measure the amount of a particular gas in a sample that is changing with time. Among these experiments are those which are concerned with the measurement of gas that is diffusing out of a solid. In many cases if the time rate of evolution of gas from the solid can be measured, the diffusion coefficient can be calculated. The mass spectrometer is particularly well suited for making this type of measurement for three reasons. (1) It is selective and therefore can be used to measure only the gas with which the experiment is concerned. (2) It has a high sensitivity and therefore can measure very small diffusion rates. (3) Under the conditions of this type of experiment it is stable; i.e., the sensitivity will remain constant for long periods of time.

Gentner and Trendelenberg¹ were perhaps the first to show that one could measure diffusion coefficients with the mass spectrometry.

ter but the mathematical treatment of the process was expanded and the methods improved by Van Wieringen and Warmoltz,² and also by Frank, Swets, and Fry.³ In any experiment in which the mass spectrometer is used to measure a gas pressure that is changing with time it takes a finite length of time for the gas to leave the area from which it is evolving or being generated and to pass down into the mass spectrometer ion source. Therefore it is essential that the rate at which the pressure is changing with time be slow compared to the rate at which the gas is pumped out of this inlet system through the ion source. This means that the container in which the diffusion specimen is mounted must be small and mounted as close to the ion source as possible. All connecting tubing must be large and have a high conductance, which also means that no controlled leak should be used.

In the case where the sample to be measured consists of gas which has diffused out of a solid it is necessary to solve the diffusion equations with the appropriate boundary conditions and from the solution find an expression for the rate at which gas is diffusing out of the solid. The diffusion coefficients are determined by comparing the curves obtained experimentally using the mass spectrometer with those obtained from the mathematical expressions. One of the most common ways to study the diffusion of gases in solids is to use a thin flat plate of the solid as a boundary between the gas to be studied and the vacuum system of the detecting device. In this kind of experiment a small vacuum tight chamber is attached to the mass spectrometer with a tube connecting the inside of this chamber directly to the ion source. One wall of this chamber is made up of a thin flat plate of the solid to be studied. On the outside of this flat plate there is usually another chamber which contains the gas to be studied. When the gas is introduced into this outside chamber it diffuses through the solid into the mass spectrometer.

The technique for measuring the diffusion coefficients is the following: The chamber outside of the specimen is evacuated. Then the gas is suddenly introduced and the pressure held constant until steady state diffusion through the plate is achieved. The rate of diffusion into the mass spectrometer appears to be delayed for a short period of time, then rises slowly, and eventually levels off at steady state. If the time constant for the rate at which gas is pumped out of the chamber through the ion source is very small compared to the time required for steady state diffusion to be reached then the variation of the ion current with time is given by

$$h = h_0 + 2h_0 \sum_{n=1}^{\infty} (-1)^n e^{-n^2 \pi^2 t / l^2} \quad n = 1, 2, 3, \dots \quad (1)$$

where

$$h_0 = \frac{C_1 D S A}{F_1 l} \quad \text{and} \quad p = \frac{\pi^2}{l^2} D \quad (2)$$

C_1 is the concentration of gas atoms just inside of the solid on the outside surface, D is the diffusion coefficient and is assumed to be constant, A is the area of the plate, l is the thickness, F_1 is the conductance of the leak which is used for calibrating the instrument, and S is the sensitivity for the particular gas being studied. It is easily seen that when the time t is very large, the exponential series reduces to zero and the steady state value is just h_0 . This is the maximum rate of diffusion. If h_0 is multiplied by the experimentally determined values of F_1 and l and divided by S and A , the steady state diffusion rate is normalized to standard conditions. This is the permeation rate (P) often quoted in the literature and is given by

$$P = C_1 D \quad (3)$$

C_1 is sometimes called the solubility when the gas pressure outside of the solid is one atmosphere. If the units of F_1 and S are properly chosen, C_1 is an expression of the number of atoms dissolved per cubic centimeter in the solid lattice under the specified tempera-

ture and pressure conditions. Both C_1 and D are temperature-dependent.

When gas is suddenly removed from the outer chamber the gas in the solid diffuses both ways and the ion current decreases. The variation with time becomes

$$h = 2h_0 \sum_{n=1}^{\infty} (-1)^{n+1} e^{-n^2 \pi^2 t / l^2} \quad n = 1, 2, 3, \dots \quad (4)$$

The exponential series converges very rapidly so that after a short time only the first term is important. Thus the decay becomes a simple exponential decay. The time constant for the decay is $1/p = l^2/\pi^2 D$ and is measured directly from the recorder trace. The thickness (l) is measured separately so the diffusion coefficient is easily calculated.

The diffusion coefficient can also be determined from the curve obtained when gas is being introduced into the solid. The method used earlier by Van Wieringen and Warmoltz² and also by Frank, Swets, and Fry³ was that of comparing the experimental curve with a series of theoretical curves obtained from Equation (1). The theoretical curves all have the same h_0 value but different p values. When a good fit is obtained between the experimental curve and a theoretical curve the p value of the theoretical curve is used to find the diffusion coefficient. This method involves the experimenter's judgment to some extent. For this reason the following modification of a method used by Barrer⁴ may be more satisfactory. If Equation (1) is integrated the result is

$$Q = h_0 t + \frac{2h_0}{p} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} [1 - e^{-n^2 \pi^2 t / l^2}] \quad (5)$$

A plot of the integral, Q , against time starts out at zero with a small slope which increases slowly with time. The curve approaches a straight line with constant slope as the exponential terms in (5) become negligible. Therefore when t is large the exponential terms drop out and (5) becomes

$$0 = h_0 t + \frac{2h_0}{p} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \quad (6)$$

which is the equation for the straight line portion of the curve. The series

$$\sum_{n=1}^{\infty} \frac{(-1)^n}{n^2}$$

has the sum $-\pi^2/12$. Extrapolating the straight portion of the curve to the $Q = 0$ axis the intercept is obtained from

$$0 = h_0 t_0 - \frac{\pi^2 2h_0}{12p} \quad (7)$$

and

$$t_0 = \frac{l^2}{6D} \quad (8)$$

Therefore the experimentally obtained mass spectrometer curve can be integrated with a planimeter and the integral plotted against the time t . Then extrapolating the straight portion of the curve to the $Q = 0$ axis the value of t is just t_0 and the diffusion coefficient can be obtained from (8). This method is actually shorter than the curve matching method and requires less judgment on the part of the experimenter. If the diffusion coefficients are calculated from the two curves obtained when gas is introduced into the solid and when it is simply evolving from the solid it is possible to check to see if the diffusion coefficients are varying with time.

McAfee⁵ has developed another method for calculating the diffusion coefficients from the curve described by Equation (1). He found that a straight line drawn parallel to the curve through the inflection point intercepts the time axis at

$$t_1 = \frac{l^2}{\pi^2 D} \left(i - \frac{e-2}{2e} \right) \quad (9)$$

where e is again the natural logarithm base. The t_1 is measured on the experimental curve obtained with the mass spectrometer and the diffusion coefficient easily calculated from Equation (9). This method is shorter than that described above but requires a little

more judgment on the part of the experimenter.

Another important advantage of using the mass spectrometer to measure the diffusion coefficients of gases in solids is that it can be used to study the isotope effect. Frank, Lee, and Williams⁶ showed that it was possible to measure simultaneously the diffusion coefficients for both hydrogen and deuterium diffusing in steel by using the mass spectrometer as a detecting device.

REFERENCES

1. GENTNER, W. AND TRENDLENBERG, E. A., *Z. Naturforschung.*, **9**, 802 (1954).
2. WIERINGEN, A. VAN AND WARMOLTZ, N., *Physica*, **22**, 849 (1956).
3. FRANK, ROBERT C., SWETS, DON E., AND FREY, DAVID L., *J. Applied Phys.*, **29**, 892 (1958).
4. BARBER, R. M., "Diffusion in and through Solids," p. 222, Cambridge University Press, New York, 1941.
5. MCAFEE, KENNETH B., JR., *J. Chem. Phys.*, **28**: 218 (1958).
6. FRANK, ROBERT C., LEE, ROBERT W., AND WILLIAMS, ROBERT L., *J. Applied Phys.* **29**, 898 (1958).

ROBERT C. FRANK

GAS CHROMATOGRAPHY IDENTIFICATIONS

Although still relatively young, gas chromatography has already developed into one of the most powerful adjuncts of spectroscopy. By itself the technique is capable of separating individual components from highly complex mixtures and providing precise quantitative estimates of their concentrations. When spectroscopic techniques are utilized for identifying the isolated components, an analytical system of remarkable abilities is provided.

While the method was applied in principle for many years, it displayed rapid growth only after James and Martin¹ published their work on gas-liquid partition chromatography in 1952. As with other chromatographic methods, a two-phase system is involved. The stationary phase in this case is

contained within the column either as a solid (adsorption chromatography) or as a liquid held by a solid support or on the column wall (partition chromatography). The mobile phase is a gas which carries the sample through the column. Phase equilibria occur between the sample components and the mobile-stationary phases. Individual components are distributed, or partitioned, between the two phases to differing degrees and become separated.

In some instances the equilibria depend upon boiling point differences in much the same manner as found in conventional distillation columns. In others, various chemical forces are involved which supplement the boiling point effect. Regardless of the nature of the forces however, chromatographic columns can usually be designed to be many times more effective than distillation procedures.

The sample is injected into the gas chromatograph either as a gas or as a liquid which immediately volatilizes within the inlet. From here it moves with the carrier gas into the chromatographic column where the phase equilibria are established. In elution analysis the carrier gas is a continuous flow which moves the individual components through the column, usually at different rates. At the exit of the column the stream enters a detector which responds differently to sample components than it does to carrier gas. The output of the detector is then displayed on a recorder to give a chromatogram such as that shown in Figure 1.

The time required for a given component to pass through a column under appropriate flow rate and temperature conditions can be used for identifying the component. The height or area of the recorded peak can be used for establishing its concentration. Thus gas chromatography can be utilized for both qualitative and quantitative analysis.

The strong relationship between the technique and spectroscopy arises from several factors. Chromatographic separations sim-

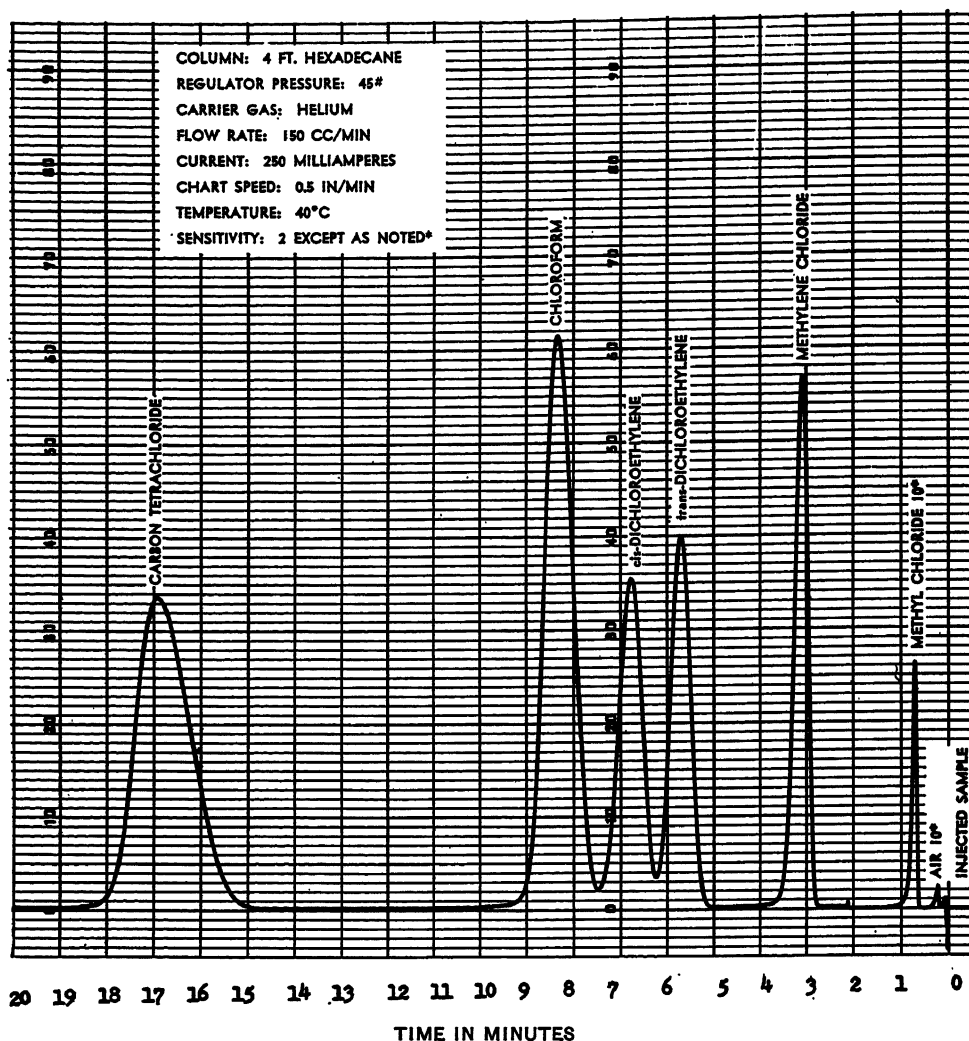


Fig. 1. Chromatogram of chlorinated hydrocarbon mixture.

plify samples examined spectroscopically and provide highly purified samples for calibration purposes. On the other hand, spectroscopic methods are often required to identify chromatographic fractions which cannot be determined by elution times alone. Numerous papers have been presented²⁻¹² which demonstrate the effectiveness of the combined system. Difficulties arising because of the minute samples normally used in chromatography have been overcome for the most part by development of microsampling

techniques in spectroscopy and the use of preparative scale chromatographic columns.

Galloway and Johns⁶ in 1957 showed that a positive identification of sample components can be made with a mass spectrometer by flowing the effluent from the gas chromatograph directly into the mass spectrometer. (Gohlke⁷ also employed this technique using a mass spectrometer with an extremely fast scan time. If the mass spectrometer cannot be connected directly to the gas chromatograph or the scan time is too slow, the

sample components can be collected and identified later.

Collection of the sample components is still almost always required when infrared is used for identification. Since infrared usually requires a larger sample than a mass spectrometer it is also important that a large enough sample can be charged into the gas chromatograph to permit collection of enough of the component of interest. This problem as already indicated is being solved by decreasing the amount of sample needed for infrared (see "Infrared Microscopy" in "Encyclopedia of Microscopy") and/or increasing the amount of sample which can be handled by gas chromatography. The technique of using infrared for the qualitative analysis of very small fractions from a gas chromatograph was described in 1958 by Gallaway *et al.*⁶; and Carle and Johns described the design and application of preparative scale gas chromatography for increasing sample size.

At present there is still considerable development work in progress on such aspects as high sensitivity detectors, more efficient columns, high temperature applications, and many others. Fortunately, the literature coverage has been excellent through rapid publication of symposia papers^{13, 14, 15} and texts.^{16, 17, 18, 19} These references especially the very complete Manual¹⁹ should be consulted for a more comprehensive treatment of this subject.

REFERENCES

1. JAMES, A. T., AND MARTIN, A. J. P., *J. Biochem.*, **50**, 679-90 (1952).
2. ANDERSON, O. M. W., *Analyst*, **84**, 50 (1959).
3. BELLIS, H. E., AND SLOWINSKI, E. J., JR., *J. Chem. Phys.*, **25**, 794 (1956).
4. DOERING, W. H. T., *J. Opt. Soc. Am.*, **45**, 227 (1955).
5. EVANS, D. E. M., AND TALLOW, J. C., *J. Chem. Soc.*, **1955**, 1184.
6. GALLAWAY, W. S., AND JOHNS, T., Paper No. 88, 1957—Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

7. GOHLKE, R. S., Paper No. 142, 1958—Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.
8. KARR, C., JR., BROWN, P. M., ESTEP, P. A., AND HUMPHREY, G. L., *Fuel*, **37**, 227 (1958).
9. Ibid., *Anal. Chem.*, **30**, 1413 (1958).
10. LIBERTI, A., COSTA, G., AND PAULUZZI, E., *Chimico e industria*, **38**, 674 (1955).
11. PATTON, H. W., LEWIS, J. S., AND KAYE, W. I., *Anal. Chem.*, **27**, 170 (1955).
12. YVES, R. N., *Perfumery and Essential Oil Record*, **49**, 290 (1958).
13. DESTY, D. H., ed., "Vapour Phase Chromatography," Academic Press, New York, 1956.
14. DESTY, D. H., ed., "Gas Chromatography," Academic Press, New York, 1958.
15. COATES, V. J., NOEBELS, H. J., AND FAGERSON, I. S., ed., "Gas Chromatography," Academic Press, New York, 1958.
16. PHILLIPS, C. S. G., "Gas Chromatography," Academic Press, Inc., New York, 1956.
17. KEULEMANS, A. I. M., "Gas Chromatography," Reinhold Publishing Corp., New York, 1957.
18. PECSON, R. L., ed., "Principles and Practice of Gas Chromatography," John Wiley & Sons, Inc., New York, 1959.
19. JOHNS, T., "Gas Chromatography Applications Manual," Beckman Instruments, Inc., Fullerton, California, 1959.

WILLIAM F. ULRICH

ISOTOPE RATIO DETERMINATION. See p. 210.

LOW IONIZING VOLTAGE ANALYSIS OF COMPLEX ORGANIC MIXTURES

Mass spectrometric analysis with low-ionizing voltage refers to the use of reduced energy electrons to produce a spectrum consisting primarily of molecular ions. While the actual ionizing voltage used depends upon the species being investigated, the ionizing voltage generally is adjusted to a value in excess of the appearance potential of the molecular ion(s), but less than the appearance potential of fragment ions resulting from bond fission.

There are four broad limitations in the application of mass spectrometry to the analysis of organic compounds: (1) instru-

MASS SPECTROMETRY

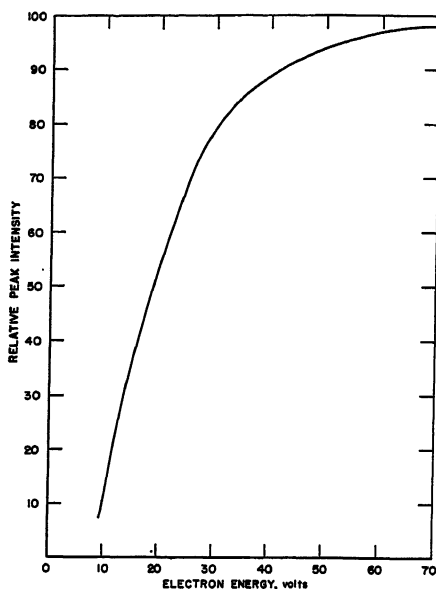
ment resolving power, (2) vapor pressure of the sample, (3) stability of the sample under high vacuum and elevated temperature conditions, and (4) spectral interferences. Spectral limitations arise from the similarity of fragmentation patterns for organic compounds of different structural types, various species having the same molecular weight, and rearrangement ions that in many instances correspond in mass to the molecular weight of lower members of a homologous series. The use of low-energy electrons will in many instances circumvent these difficulties.

The first application of this technique (reported in the literature in 1950) was by Stevenson and Wagner to the mass spectrometric determination of mono-deutero paraffins. Since 1957 this technique has been widely adopted in petroleum and chemical laboratories. Low-ionizing voltage operation has been applied to both qualitative and quantitative determinations of organic components in complex liquid mixtures. In many instances only the molecular weights of the compounds present can be determined. For some mixtures the structural types can be determined, but a quantitative analysis is not possible, as calibration data are not available. However, for many aromatic, olefinic, and phenolic type compounds cali-

TABLE 1. APPROXIMATE IONIZATION POTENTIALS FOR VARIOUS HYDROCARBON COMPOUNDS

Compound class	Ionization potential (electron volts)
<i>n</i> -Paraffins ($C_3 \rightarrow C_{10}$)	11.2 $\rightarrow$ 10.2 e.v.
1-Olefins ($C_4 \rightarrow C_{10}$)	9.7 $\rightarrow$ 9.5
Aromatics (C_6H_6) (lower as alkyl groups are added)	9.5
Dissociation energies: Additional energy to produce fragmentations*	
D (C—C) $\sim$ 3.3 e.v.	
D (C—H) $\sim$ 4.2	

* Reduced by rearrangements, etc., in certain instances.



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FIG. 1. Typical ionization efficiency curve for molecular ions from hydrocarbons.

bration data are available, and quantitative determinations can be made. In detecting impurities in relatively pure compounds there are advantages to obtaining a spectrum at low-ionizing voltage. For many structural types it is difficult to determine the presence of impurities having molecular weights lower than the major component, as rearrangement ions from the major component can occur at lower mass numbers. Many of these rearrangement ions can be eliminated at low-ionizing voltage, thus making detection of impurities possible.

Instrument Operation. As shown in Table 1, compound types can be grouped roughly according to ionization potentials with the olefinic and aromatic types requiring the least energy to produce ionization. Many fragment ions from organic molecules require several volts additional energy compared with the molecular ion. Thus, the ionizing voltage can be adjusted to produce a spectrum consisting primarily of the parent ions of the compound types present. Elec-

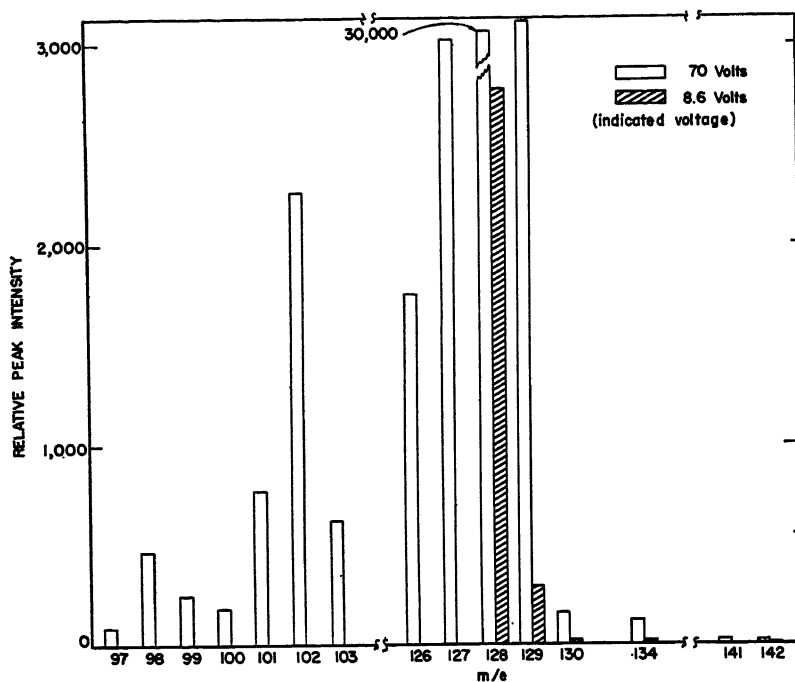
tron accelerating electrodes are normally operated (~ 70 volts) considerably above the appearance potentials of the singly- and doubly-charged ions from hydrocarbons. As shown in the ionization efficiency curve, Figure 1, this results not only in more intense peaks but also in more stable operation, as any variation in electron accelerating voltage will have a minimum effect on peak intensity. Both of the above advantages are lost by operating at reduced ionizing voltages. The slope of the ionization efficiency curve is much larger for example, at 10 volts, and also the peak intensity will be reduced for a given sample charge. The actual reduction in peak intensity will depend on the shape of the ionization efficiency curve for the particular compound being investigated. When molecular ion data obtained at 10 volts are compared with those obtained at 70 volts, reductions in peak intensities the order of a factor of 10 are quite common. This can in many instances be compensated for by increasing the sample charge. Circuit changes necessary to operate commercially available mass spectrometers at reduced ionizing voltages have been described by Lumpkin⁸.

Application. The technique is most effective when applied to a mixture consisting of similar structural types. For a hydrocarbon mixture it is desirable to have saturated and unsaturated structures separated before the analysis. However, in certain instances it is possible to determine whether a particular peak is assignable to a saturated or unsaturated structure on the basis of spectra obtained at progressively lower ionizing voltages. For hydrocarbon mixtures containing few if any oxygenated compounds and boiling below approximately 200°C , prior analysis for group types is feasible and very useful. As only drop quantities are required for the mass spectrometric determination, samples can be collected directly from a fluorescence indicator chromatographic column for spectrometric investigation. In

this manner the low-ionizing voltage technique can be used most effectively, and at the same time total values for the saturates, olefins, and aromatic structural types can be determined. Molecular ions observed in the spectra of these three fractions can then be associated with structures of the appropriate hydrocarbon classes. Identical molecular ion series occur for several classes of compounds—one example being ketones, aldehydes, and paraffins. A second overlapping series occurs for the olefins and naphthenes.

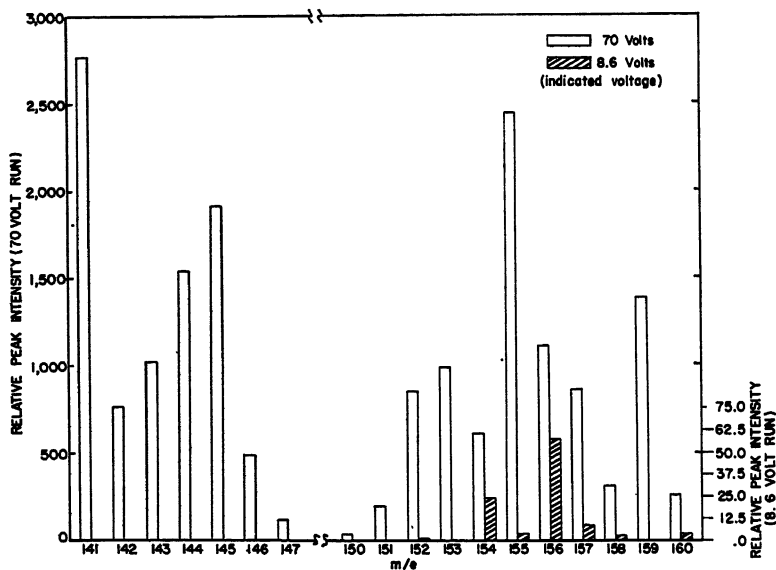
Figure 2 shows a comparison of naphthalene spectra obtained at ionizing voltages of 70 and 8.6 volts. The 8.6 volts is the indicated value, with the actual voltage being approximately 10.6 volts. In addition to the molecular ion peak, the only other peaks appearing in the 8.6-volt spectrum are from C^{13} isotopes and from impurities in the naphthalene. Impurity peaks can be seen at masses 134 and 142. Fragmentation peaks in the mass range 97 to 127 are completely missing in the spectrum obtained at low-ionizing voltage. As all even mass peaks could be molecular ions resulting from compounds containing various combinations of carbon and hydrogen, peaks occurring at masses 126, 102, 100, and 98 in the spectrum of naphthalene can be misleading. In general, rearrangement ions appearing at even masses and corresponding in mass to a radical plus a hydrogen atom have appearance potentials only a few tenths of a volt higher than the parent molecular ion. For this reason rearrangement ions cannot always be eliminated from the spectrum; however, in mixtures of high-molecular weight hydrocarbons all parent mass peaks of interest are above mass 100 and lower mass fragment peaks can be tolerated. An example of the application of the low-ionizing voltage technique to a hydrocarbon mixture is shown in Figure 3. This sample is an aromatic fraction of a neutral oil from the hydrogenation of coal. The normal mass spectrum shows peaks at almost every mass number, and it would be ex-

MASS SPECTROMETRY



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FIG. 2. Partial mass spectrum of naphthalene, normal and reduced ionizing voltages.



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FIG. 3. Partial mass spectrum of a 260-276°C aromatic fraction of a neutral oil from the hydrogenation of coal.

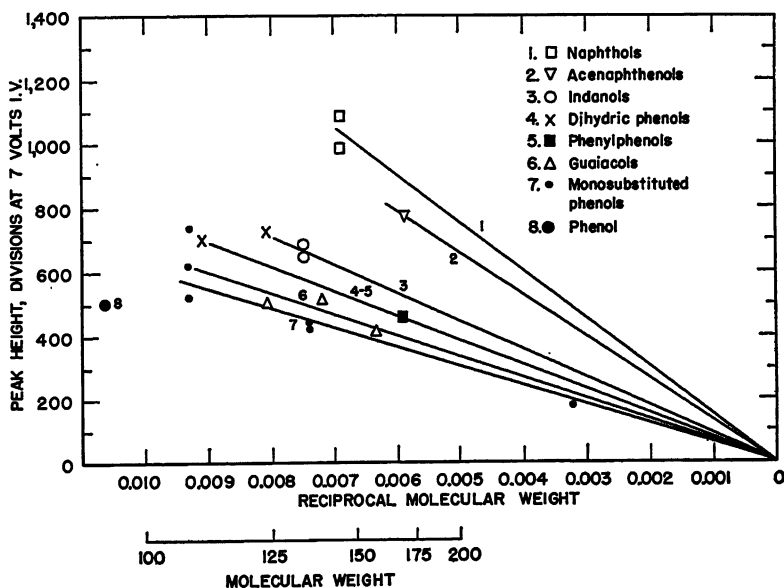
LOW IONIZING VOLTAGE ANALYSIS OF COMPLEX ORGANIC MIXTURES

tremely difficult to determine even a molecular-weight range for the compounds present. This information can be easily derived from the spectrum obtained at reduced ionizing voltage. The first parent mass indicated is mass 152 with the most intense peak, mass 156, corresponding to an ethyl or dimethyl substituted naphthalene. Peaks showing at odd mass numbers are not fragmentation peaks in this instance; rather they are due primarily to C^{13} isotope. The complete low-voltage spectrum of this unknown sample contains 22 parent mass peaks, indicating a minimum of 22 compounds present in this 16°C fraction. This is a minimum number of compounds, as individual isomers cannot be identified by the low-voltage method.

This technique also can be applied to the quantitative analysis of complex mixtures provided a prior separation of compound types has been carried out. Lumpkin⁸ has observed that sensitivity factors for many homologous series of aromatic hydrocarbons can be determined from the sensitivity factor for the initial member of these series. In

general, sensitivity factors (chart-divisions per unit liquid volume of sample) for aromatic hydrocarbons increase with the number of ring systems and decrease with the length of alkyl substituents. Sensitivities also increase with the number of ring substituents. These correlations also apply to the corresponding phenolic-type compounds. Approximate sensitivity factors over a wide molecular-weight range can be obtained by extrapolating from the sensitivity value for the first member of the series to zero sensitivity at infinite molecular weight, as shown in Figure 4. Crable, Kearns, and Norris⁸ have correlated sensitivity factors for aromatic hydrocarbons with the type of substituent group on the ring(s).

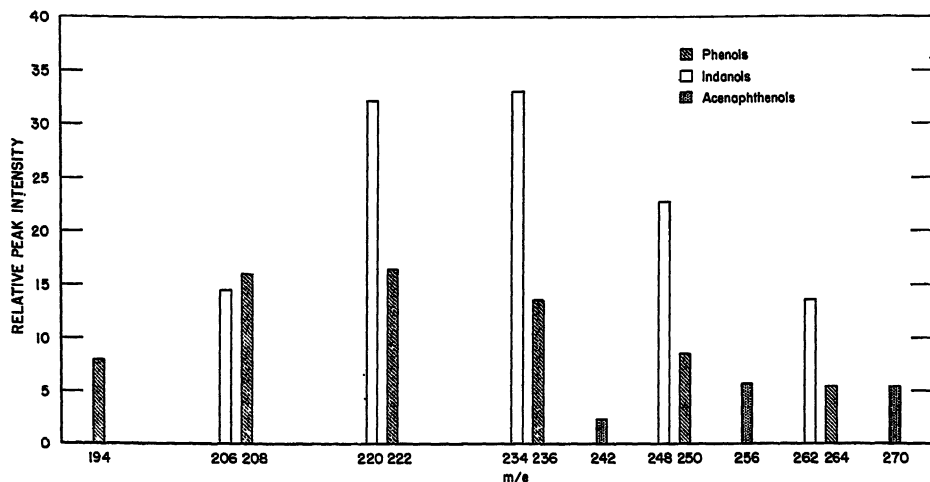
The technique is particularly useful in obtaining carbon-number distribution data for mixtures not analyzable by other methods. Carbon-number distribution data for many light oils, such as some of the common jet fuels, can be obtained by this method. Application of this method to a complex mixture of phenolic-type compounds is illustrated



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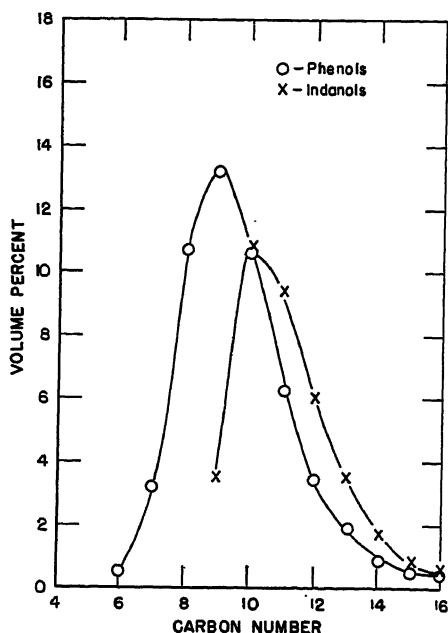
FIG. 4. Low-ionizing voltage sensitivity data for tar acids.

MASS SPECTROMETRY



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Fig. 5. Mass spectrum of trimethylsilyl ether derivative; phenol fraction (b.p. 273–340°C) of middle oil from hydrogenation of lignite (ionizing voltage 7 volts, indicated).



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Fig. 6. Low-ionizing voltage mass-spectrometer analysis. Carbon-number distribution of phenols and indanols in tar-acid fraction produced by hydrogenation of coal.

in Figure 5. In this instance the trimethylsilyl ether derivative sample was prepared to confirm the presence of the phenolic types. This resulted in a shift of 72 mass units for each hydroxyl group present in the molecule and eliminated interference from any neutral material occurring on the same mass series. Quantitative carbon-number distribution data can be obtained from the spectrum of the original sample using sensitivity data shown in Figure 4. This is illustrated in Figure 6 where data were obtained for phenols and indanols in the tar-acid fraction of oil from the hydrogenation of coal. Components containing 6 to 16 carbon atoms were found, and in a mixture of this type as little as a few tenths of a per cent is detectable at the higher carbon numbers. Data of this type are useful not only in determining the structural types present but also the extent of alkyl substitution on these structures and average molecular weights. In some instances these data have been used for comparison with the total value for the individual isomers at each carbon number, as determined by chemical and other methods. This technique not only results in faster determinations than by classical methods but also

provides information not obtainable from other sources.

BIBLIOGRAPHY

1. STEVENSON, D. P., AND WAGNER, C. D., *J. Am. Chem. Soc.* **72**, 5612 (1950).
2. FIELD, F. H., AND HASTINGS, S. H., *Anal. Chem.*, **28**, 1248 (1956).
3. LUMPKIN, H. E., *Anal. Chem.*, **30**, 321 (1958).
4. SHARKEY, A. G., JR., WOOD, GORTON, AND FRIEDEL, R. A., *Chem. and Ind.*, 833 (June 28, 1958).
5. SHARKEY, A. G., JR., WOOD, G., SHULTZ, J. L., WENDER, I., AND FRIEDEL, R. A., *Fuel*, **38**, 315 (1959).
6. KEARNS, G. L., MARANOWSKI, N. C., AND CRABLE, *Anal. Chem.*, **31**, 1646 (1959).
7. SHARKEY, A. G., JR., ROBINSON, C. F., AND FRIEDEL, R. A., "Advances in Mass Spectrometry," Ed. J. D. Waldron, Pergamon Press, London, 1959, pp. 193-208.
8. CRABLE, G. F., KEARNS, G. L., AND NORRIS, M. S., *Anal. Chem.*, **32**, 13 (1960).

A. G. SHARKEY, JR.

PETROLEUM OIL ANALYSIS

Of the many applications of mass spectrometry, one of the most interesting and industrially useful is the analysis of petroleum products. Mass spectrometry was first used in the petroleum industry in 1942 as a method of analyzing refinery gas streams.^{7, 8, 10, 63, 64} Within a few years, mass spectral methods had been developed for the determination of hydrocarbon types of gasoline fractions,^{8, 9, 34} and by that time the mass spectrometer had become an essential analytical tool for petroleum refineries. The next major development was a heated inlet system,^{10, 45} which made possible the mass spectral study of high-boiling petroleum fractions. It is the purpose of the present article to review the status of high-temperature mass spectrometry and its application to the study of the composition of distillate petroleum fractions boiling above the kerosene range. In writing this review, the authors have made liberal use of two of their earlier reviews on the subject.^{30, 48}

Instrumental

Standard single-focusing analytical mass spectrometers⁶⁸ have been modified for high-molecular-weight applications by adding a heated inlet system and by making minor alterations to the ion optical system to resolve the mass scale up to about mass 600.^{10, 12, 35, 42, 45, 60} The difficulties attendant upon maintaining a metal high-vacuum inlet system at high temperature have generally led to the use of glass systems in which molten metal, such as gallium, tin, or indium, is used for vacuum-control valves and for sealing sintered-glass discs for sample introduction.^{12, 35, 42, 45} Such systems can be operated up to about 500°C with no difficulty. For the analysis of hydrocarbons, an inlet-system temperature of about 350°C will vaporize compounds containing up to about fifty carbon atoms per molecule without thermal decomposition. Materials susceptible to thermal degradation (many nonhydrocarbons) must be run at lower temperatures, and this, of course, limits the use of the technique to the lower-boiling compounds. When only moderate temperatures are required, systems having "Teflon" valve seats, packing, etc.,^{10, 14} can be employed up to about 200°-250°C.

In order to resolve the mass peaks in the 200 to 600 mass range, it is necessary to decrease the size of the ion definition and resolution slits in comparison to that used in a standard analytical mass spectrometer. This, of course, results in a loss of sensitivity which must be compensated for by increasing amplifier gain on the ion detector. Vibrating-reed amplifiers have been widely used in this application, since they possess the required high gain coupled with excellent stability. Other instrument modifications for operating in the higher mass range are largely concerned with providing the necessary flexibility and stability of instrument operation.^{12, 45}

Resolution above 1 in 600 can be accomplished by double-focusing mass spectrometers. Several instruments of this type,

suitable for organic analysis, have been described,^{19, 62} and the modifications and use of one of these for the analysis of heavy petroleum fractions has just been reported.¹⁶

Digitization of the mass spectra of high-molecular-weight materials is accomplished by means similar to those used in low-mass work. Procedures for data reduction, therefore, vary from manual to completely automatic. The calculation of the composition of heavy petroleum fractions is quite detailed and is usually carried out on high-speed automatic computers.

Mass Spectra

The application of mass spectrometry to the study of composition of heavy petroleum fractions requires the availability of a variety of reference spectra. It is important to have mass spectra of pure compounds, particularly those believed to be typical of petroleum molecules, and mass spectra of narrow-type concentrates of petroleum origin.

Neither the pure compounds nor the narrow concentrates are available to the extent and variety needed, but the available calibration materials have been sufficient for the development of mass spectral methods for studying many aspects of molecular composition of heavy distillate oils. The pure com-

pounds on which many of the present methods have been based are primarily those synthesized by American Petroleum Institute Research Projects 42, 48, and 52. Mass spectra of these API compounds are included in the spectral tables distributed by API Research Project 44. Inasmuch as the spectra of many high-molecular-weight compounds have been discussed in detail in the literature,^{8, 11, 13, 24, 40, 45, 46, 53, 54} only a brief review of the more important generalizations drawn from the spectra is given here to show the typical spectral variations among molecular types and therefore to indicate the general basis of the mass spectrometric analytical methods for studying heavy-oil composition.

Hydrocarbons. The simplest mass spectra of heavy hydrocarbons are those of the *n*-alkanes, and the spectra of all the members of that series are, in general, quite similar. The spectrum of *n*-tetracosane is shown as a bar graph in Figure 1 as an example. In the figure, the large peak occurring at mass 338 is referred to as the "parent peak," since it represents the ions formed from the parent molecules ($C_{24}H_{50}$) by the loss of a single electron. The peaks appearing at mass numbers 339 and 340 are the heavy-isotope equivalents of the parent peak, since they

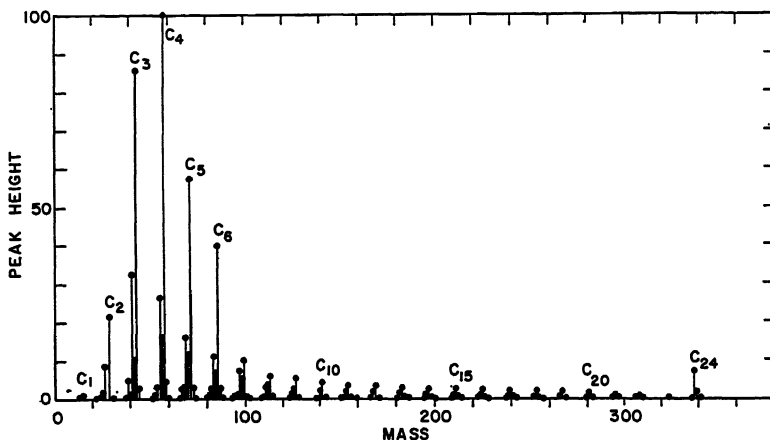
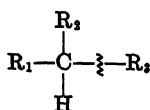


Fig. 1. Mass spectrum of *n*-tetracosane. (Redrawn from O'Neal and Wier⁴⁵ with permission of the American Chemical Society.)

are positively charged parent molecules ($C_{24}H_{50}$) containing, respectively, one or two heavy atoms (H^2 , C^{13}). The many peaks occurring below the parent peak are all formed by fragmentation of the molecule, and they are usually referred to as "fragment peaks." The most pronounced of the fragment peaks in the spectrum of *n*-tetracosane are C_nH_{2n+1} alkyl peaks in the C_2 -to- C_6 region, and this is typical of the mass spectra of heavy *n*-alkanes.

The spectra of isoalkanes are similar to those of *n*-alkanes, except that parent peaks are usually negligible, and large C_nH_{2n+1} peaks occur at carbon numbers equivalent to the loss of any one of the alkyl groups attached to the tertiary (or quaternary) carbon atom of the molecule, as indicated below.



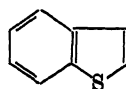
The loss of an alkyl substituent in this manner is ordinarily accompanied, to an appreciable extent, by the loss of an additional hydrogen atom, with the result that a sizeable spectral peak occurs at a mass one less than that of each major C_nH_{2n+1} fragment peak.

The largest peaks in the spectra of cycloalkanes are generally those due to the loss of one or more alkyl groups from tertiary or quaternary carbon atoms of the ring. As in the case of isoalkanes, the loss of an alkyl group is accompanied, to a considerable extent, by the loss of a hydrogen atom. Therefore, the large fragmentation peaks in spectra of monocycloalkanes appear on the C_nH_{2n-1} and C_nH_{2n-2} series. In polycycloalkanes,^{39, 49, 52} fragmentation is more complex because of the tendency of certain types of ring systems to break apart. Otherwise, the major peaks are the parent peaks and the fragment peaks of equal or slightly greater carbon numbers than those of the condensed nuclei of saturate rings.

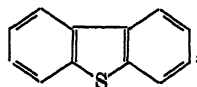
The most significant peaks in the spectra of aromatic compounds are those from the

loss of an alkyl group due to fragmentation at the weak bond between the α and β carbon atoms of a nuclear substituent. In this type of fragmentation, there is a strong tendency for the resulting fragment to contain an extra hydrogen atom. Therefore, the spectrum of *n*-decylbenzene, for example, gives a very large fragment peak not only at mass 91 (benzyl or tropylium⁵⁵), but also at mass 92 (toluene). Parent peaks are large and are thus particularly useful in mass spectra of aromatic hydrocarbons.

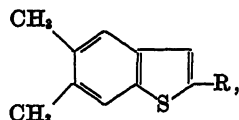
Nonhydrocarbons. The mass spectra of thiopheno compounds, e.g., alkyl derivatives of benzothiophene



and dibenzothiophene



are similar in many respects to spectra of aromatic hydrocarbons. For example, the parent peaks of alkyl benzothiophenes occupy the same mass series (C_nH_{2n-6}) as alkyl benzenes. Similarly, major fragment peaks of benzenes and benzothiophenes have the same mass series (C_nH_{2n-7}). However, the major fragment peaks differ by the equivalent of four carbon atoms on the C_nH_{2n-7} series because of the difference in size of the condensed nucleus. For example, the major fragment of a trialkyl benzothiophene of the type



where R is a long alkyl chain, appears on the C_nH_{2n-7} series at mass 175, whereas the equivalent trialkyl benzene fragment appears at mass 119. This behavior is used to advantage in analytical schemes for distin-

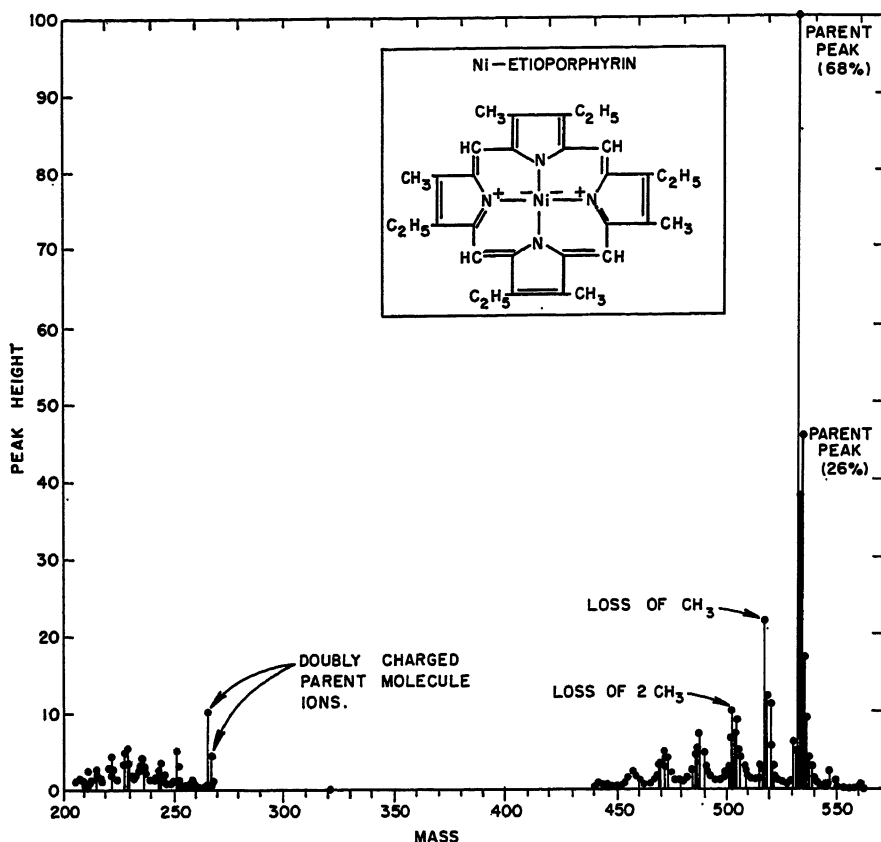
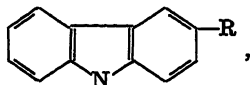


FIG. 2. Mass spectrum of nickel-etiochlorophyllin.

guishing between any aromatic hydrocarbon type and its thiopheno derivative.

Nitrogen compounds containing an odd number of nitrogen atoms can be distinguished from hydrocarbons because the mass numbers of their parent ions are odd rather than even and the mass numbers of their fragment peaks are even rather than odd. For example, alkyl carbazoles.



have parent masses on the C_nH_{2n-15} series and major fragments on the C_nH_{2n-18} series. Porphyrin-metal complexes, which contain four nitrogen atoms, are remarkably stable and volatile and therefore can be studied by

conventional high-mass spectrometers. Their spectra are characterized by large parent peaks and smaller fragment peaks resulting from the loss of short side chains. The parent-peak distribution corresponds to the isotope distribution of the specific metal of the porphyrin complex. The spectrum of nickel-etiochlorophyllin* is shown in Figure 2.

Oxygenated compounds in heavy petroleum oils have not been as extensively studied as have nitrogen and sulfur compounds and hydrocarbons. The mass spectrometer can, however, be used for characterizing oxygen-containing compounds of high molecular weight, as demonstrated for fatty

* The sample of nickel-etiochlorophyllin was prepared by Dr. A. H. Corwin of Johns Hopkins University.

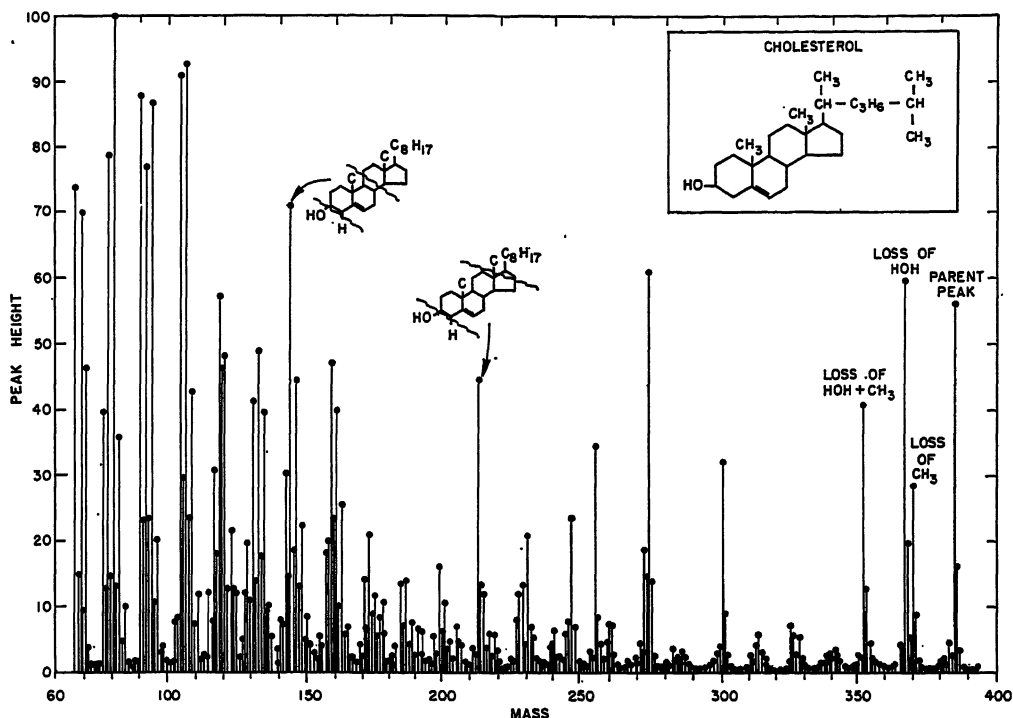


FIG. 3. Mass spectrum of cholesterol.

acids,^{4, 26, 44} esters,^{3, 13} alcohols,¹¹ glycols,^{53, 54} phenols,⁵⁵ and steroids.²⁴ This is illustrated in Figure 3 by the mass spectrum of cholesterol. Characteristic fragmentation modes for this sterol involve the loss of HOH and a methyl group, presumably one of the angular methyl groups. Many of the prominent peaks involve ring rupture in combination with the loss of HOH and/or a methyl group, as shown in Figure 3. Spectral changes can be correlated with the type of side-chain substituent, the degree of saturation of ring B, and the presence or absence of an OH group in ring A.

One aspect of mass spectra which makes them useful for identification of compounds is that each compound of a given empirical formula has a unique distribution of heavy-isotope equivalents of the parent peak. For example, Table 1 shows the spectral peak heights at masses 129 and 130 for eight compounds having parent peaks of mass 128.

TABLE 1. ISOTOPIC ABUNDANCES OF SOME COMPOUNDS HAVING PARENT PEAKS OF MASS 128

Empirical Formula	Peak Height, % of Parent-Peak Height	
	129	130
C ₁₀ H ₈	10.93	0.54
C ₉ H ₂₀	10.03	0.45
C ₈ H ₁₆ O	8.93	0.55
C ₈ H ₄ N ₂	9.44	0.39
C ₈ H ₄ O ₂ S	6.34	5.02
C ₈ H ₆ O ₂ N ₂	6.33	0.58
C ₈ H ₄ O ₄	5.62	0.94
C ₈ H ₄ O ₂ N ₂	5.23	0.72

Lumpkin and Nicholson⁵⁸ made use of such differences in isotopic abundances in identifying products from the oxidation of *o*-xylene.

Standardization of Spectra. In order to obtain maximum usefulness from mass spectra, it should be possible to compare di-

rectly any peak of one spectrum with any peak of another spectrum. Until recently, the usual way of comparing spectra of high-mass compounds in this way was to correct each spectrum for the observed sample size and instrument sensitivity by comparing it with the spectrum of an equal amount of a standard pure compound (e.g., $n - C_{16}$) which was run the same day. This approach has not been completely satisfactory. Recently, a more useful approach has been suggested by Crable and Coggeshall¹⁸ and by Hood.²⁰ It is concerned with the use of total ionization (or total spectral peak heights) and is based on the finding of Otvos and Stevenson²¹ that total ionization per mole is proportional to the sum of the atomic ionization cross sections of a molecule. The total-ionization approach provides a correction of any high-mass spectrum for sample size and instrument sensitivity by means of a simple calculation, and it does not require any knowledge of the actual sample size or sensitivity.

A useful and simplified modification of the total-ionization technique of standardizing mass spectra has recently been adopted for use in the API Catalog of Mass Spectral Data. Each peak height of a given high-mass spectrum will be reported on the basis that the sum of the peak heights of that spectrum is a constant value, namely, 1×10^5 .

Analytical Methods

In the application of mass spectra to the analysis of heavy petroleum fractions, two general approaches can be used.^{47, 48} One is based on spectral peaks of parent-molecule ions, and the other on peaks from fragment ions. Each approach has specific advantages in certain applications, and therefore the method chosen in any particular case depends on the nature of the petroleum fraction and the type of compositional information desired.

The parent-peak method gives analyses in terms of the formula C_nH_{2n+x} , where n is

the number of carbon atoms per molecule, and x is a hydrogen coefficient which has the value +2 for alkanes and decreases by 2 for each ring and for each double bond present in the molecule. Thus, the parent-peak approach provides a determination of both a molecular-weight distribution and a hydrocarbon-type distribution.

The fragment-peak methods are based on stable fragments of lower carbon number than the original molecule, and thus they describe the components of the molecule but not necessarily the original molecule. Fragment-peak methods have the important advantage of giving a distinction between certain homologous series which have identical mass-spectral parent peaks. For example, the major alkane fragments are in the C_8 -to- C_9 region of the C_nH_{2n+1} series, whereas the alkyl naphthalene fragments are found at C_{11} to C_{14} on the mass-equivalent C_nH_{2n-18} spectral series. Likewise, as mentioned above, the major fragments of alkyl benzenes and alkyl benzothiophenes are separated by about four carbon atoms on the C_nH_{2n-7} series, whereas their parent peaks cannot be resolved with conventional mass spectrometers. It is pointed out in a subsequent section of this article, however, that new double-focusing instruments are being developed which should resolve many of these mass-equivalent parent peaks, even in the high-mass range.

Mass-spectral methods can be applied to petroleum oils having a wide range of molecular weight and molecular type. In general, however, as a sample is made more nearly homogeneous with respect to molecular weight and type by means of physical separations, more detailed information on composition can be obtained.^{20, 31, 35, 41-43, 49, 50, 56-58} For the routine analysis of oils,^{2, 48} it is usually desirable to make at least a preliminary separation into saturate and aromatic concentrates and to analyze those two concentrates individually. Inasmuch as the same separation is useful in our discussion of

the methods, the subsequent discussion of mass-spectral methods is divided into (a) the analysis of saturate concentrates, and (b) the analysis of aromatic concentrates.

Analysis of Saturate Concentrates.

Both the parent-peak and fragment-peak approaches can be used in the analysis of heavy saturate concentrates. The advantages and limitations of each are discussed below.

Parent-peak Methods. The general parent-peak approach has been described by O'Neal and co-workers.^{45, 47, 48} Briefly, it involves the comparison of heights of the various parent peaks after each has been divided by the sensitivity it would exhibit as a pure compound. The first application of the parent-peak method which O'Neal described⁴⁵ was the analysis of a paraffin wax (Figure 4). Although the original method was based on a minimum of calibration spectra of pure compounds, the analytical results were found to be quite reasonable, and the method has been used extensively^{21-23, 59, 61} with only minor modification. Very recently, the adaptation of a detailed wax method to digital computation was reported by Brown and co-workers.¹²

In the analysis of nonwax saturate concentrates, the parent-peak methods are of limited applicability because of the difficulty in differentiating between parent peaks and rearranged fragment peaks in the spec-

trum of a sample having a wide molecular-weight range. This is illustrated in Figure 5 (reference 30), which shows the spectral peak heights in the parent-peak region for a typical refinery lubricating-oil distillate and for a narrow center cut from an efficient laboratory distillation of that same refinery distillate. In the case of the laboratory distillation, it is possible to draw a base line to give an approximate distinction between parent and fragment peaks. For the refinery distillate, however, the parent peaks are camouflaged by fragment peaks, and thus a dependable parent-peak analysis is probably impossible.

For heavy petroleum saturates with a sufficiently narrow molecular-weight range, probably the best parent-peak sensitivities reported for converting from peak height to percentage composition are those of Schissler and co-workers.⁵⁷ They were based on narrow petroleum fractions and are given in Table 2.

Fragment-peak Methods. In the analysis of heavy petroleum saturates, the fragment-peak methods have the advantages of being rapid and of being applicable to even poorly distilled samples. On the other hand, the fragment methods have two minor disadvantages. One is that the low-mass fragment peaks provide no distinction between *n*-alkanes and isoalkanes. The other is that the fragment methods give saturate-ring

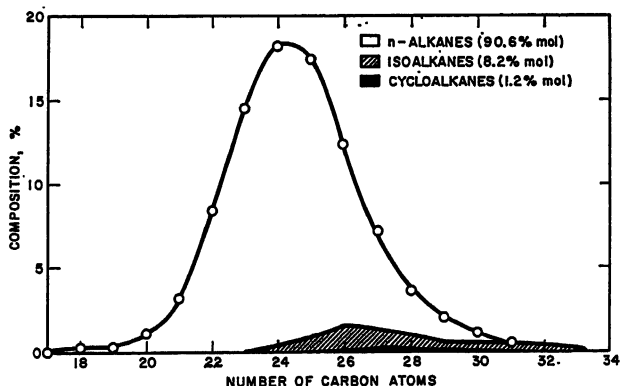
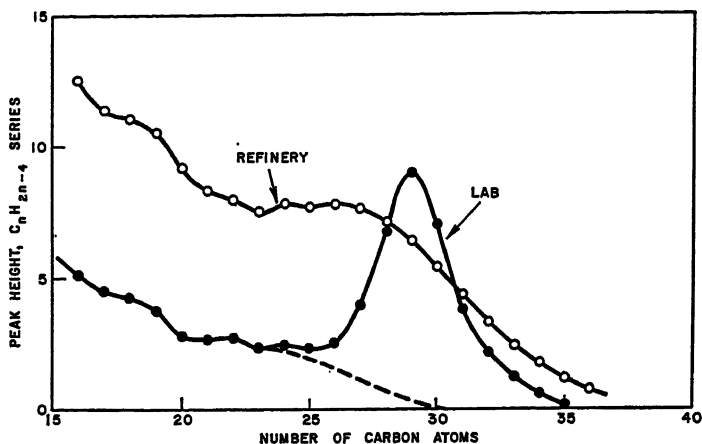


FIG. 4. Composition of a paraffin wax by mass spectrometric analysis. (Redrawn from O'Neal and Wier⁴⁵ with permission of the American Chemical Society.)

FIG. 5. Carbon-number distribution of lubricating-oil saturates.³⁰TABLE 2. PARENT-PEAK SENSITIVITIES FOR LUBRICATING-OIL SATURATES³⁷

Saturate Rings per Molecule	Parent-Peak Sensitivity
1	1.00
2	1.77
3	2.74
4	3.68
5	4.41

number analyses in terms of the number of rings per nucleus of fused rings, rather than total rings per molecule. Actually, it is probable that the fragment methods do give rings per molecule for petroleum molecules with no more than three or possibly four saturate rings, because it is now believed that essentially all of those molecules contain all of their rings in a single fused nucleus. For molecules containing five or more saturate rings, their noncondensed nature³⁰ requires the use of parent-peak methods for the determination of total rings per molecule.

Four fragment methods have been published for the mass-spectral analysis of petroleum saturates.^{17, 30, 36, 43} They have recently been compared in some detail by Hood and O'Neal,³⁰ and therefore only brief descriptions and comparisons are given below.

The earliest of these methods was that of Clerc and co-workers.¹⁷ It gives, in effect, a

determination of molecules containing zero, one, and two saturate rings, plus aromatic impurities. It is a matrix-type method based on fragments containing 4 to 11 carbon atoms. It is a convenient and useful method for the routine analysis of fractions from paraffinic crudes, but it is not applicable to saturate concentrates containing appreciable concentrations of molecules with two or more saturate rings.

Melpolder and co-workers⁴³ developed a matrix-type method which gives the relative concentration of fused-ring systems containing zero to nine saturate rings, as well as the concentration of aromatic impurities. The inclusion of seven, eight, and nine rings in the method represents a noteworthy accomplishment, but the accompanying inaccuracies sometimes produce questionable analytical results.

The third published method, that of Lumpkin and co-workers,^{28, 36} gives a determination of zero to six saturate rings per fused-ring system. This appears to be a practical ring-number range and a useful method. One disadvantage of the method is that it does not provide for the determination of aromatic impurities.

The latest method to be published, that of Hood and O'Neal,³⁰ makes use of the same

saturate mass groupings as the Lumpkin method but includes an additional mass grouping for aromatic types. The method is based on the mass spectra of essentially the same pure compounds which Lumpkin used, except that the spectra were standardized with respect to sample volume and instrumental sensitivity.²⁹ These improved spectral calibrations were found to exhibit such a strong effect of molecular weight that a separate matrix was set up for each carbon number from 16 to 32. Each matrix is actually a dual matrix which is applicable to analytical samples in which the zero-ring molecules are either mainly *n*-alkanes or mainly isoalkanes. Of the four methods, this one is the most complex, but it has the most flexibility and probably the widest applicability.

Analysis of Aromatic Concentrates.

Parent-peak Methods. The parent-peak approach is generally more useful for aromatics than for saturates because of the high parent-peak intensities exhibited by aromatic molecules. This can be seen by comparing Figure 5 with Figure 6, which shows the alkyl benzene (C_nH_{2n-6}) parent-peak series from the mass spectrum of the monoaromatics from a medium-lube refinery distillate.¹⁵

In the earliest application of the parent-peak method to heavy petroleum aromatics, O'Neal and co-workers assumed equal parent-peak sensitivities, regardless of molecular weight or molecular type.⁴⁸ The general method has now been improved by King, *et al.*,³³ who reported a comprehensive set of aromatic parent-peak sensitivities.

A recent major improvement in the aromatic parent-peak method is the use of low ionizing voltages. Gordon *et al.*,²⁵ Lumpkin,³⁷ and Kearns *et al.*³² have described the use of low voltages to overcome any masking of parent peaks by fragment peaks. This is particularly useful for concentrates containing aromatic nuclei which do not carry a long alkyl side chain. The usefulness of this new technique is illustrated in Figure 7, which shows the C_nH_{2n-26} mass-spectral series of peaks for a polyaromatic concentrate.¹⁵ The parent-peak curve obtained at the customary 70 volts is camouflaged confusingly by fragment peaks, whereas the corresponding curve obtained at an ionizing voltage of a nominal 8 volts shows the true parent-peak distribution.

Fragment-peak Methods. At least three methods have been described for determining aromatic types in heavy oils by means of fragment-peak techniques. The method of

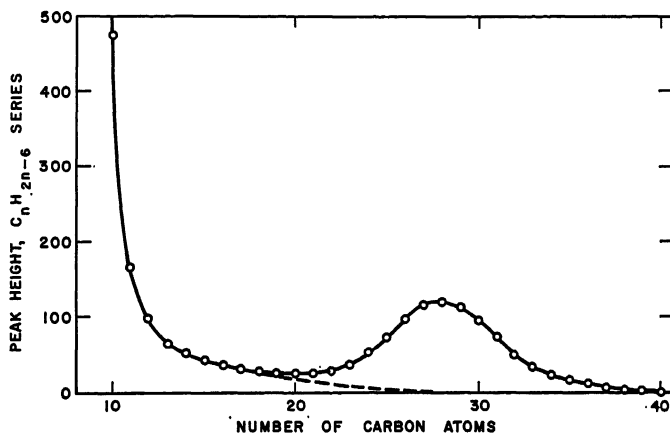


Fig. 6. Carbon-number distribution of alkyl benzenes from a medium-viscosity lubricating oil. (Redrawn from Carlson and O'Neal¹⁵ with permission of the American Society for Testing Materials.)

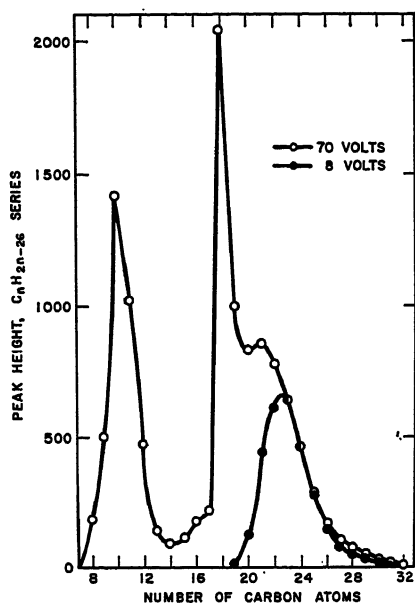


Fig. 7. Carbon-number distribution of a polyaromatic concentrate. (Redrawn from Carlson and O'Neal¹⁵ with permission of the American Society for Testing Materials.)

Hastings *et al.*²⁷ provides a means of determining twelve major aromatic types, including three types which contain thiophene rings. For each type, Hastings uses three characteristic fragment peaks. André *et al.*¹ reported a similar method for the determination of 31 types which is based on a single fragment peak being characteristic of each given type. Orkin and co-workers⁵⁰ have reported a fragment-peak method of analyzing lubricating-oil aromatics in terms of eight aromatic hydrocarbon types. No direct comparisons of these aromatic fragment methods have been made.

Application of High-Resolution High-Mass Spectrometry

The analytical methods described in the preceding section were all based on the use of conventional mass spectrometers of the single-focusing type which can resolve adjacent whole mass numbers to about mass 600. By the incorporation of double-focusing

features (both magnetic and electrostatic), it is possible to extend the resolvable mass range considerably¹⁶ and, as shown by Beynon,⁵ to resolve many ions of identical nominal mass. It therefore becomes feasible to analyze some petroleum residue fractions as well as distillate-range mixtures containing components of overlapping mass spectral series.

The exact mass of an ion of known empirical formula is calculated from the exact masses of the constituent atoms. For example, nonane and naphthalene, both of nominal mass number 128, have calculated masses of 128.1972 and 128.1033 amu (atomic mass units), respectively. Such differences in exact mass arise from the failure of the additivity law with regard to the masses of the nuclear particles. A knowledge of the exact masses is of less utility than a knowledge of the difference between exact masses, especially of ions having identical nominal mass numbers. In the example of nonane and naphthalene, this difference is 0.0939 amu. This value, observed for overlapping hydrocarbon ions, corresponds to the difference in exact mass between one carbon atom and twelve hydrogen atoms. The peak separations of some doublets which can appear in the high-resolution mass spectra of petroleum are

TABLE 3. MASS DIFFERENCE OF SELECTED DOUBLETS¹⁶

Doublet	Mass Difference ΔM , amu	Resolution Required at Mass 200, $200/\Delta M$
H ₁₂ -C	0.0939	2,130
H ₃ -D	0.0015	130,000
CH-C ¹³	0.0045	44,000
CH ₂ -N	0.0126	15,900
CH ₄ -O	0.0364	5,500
N ₂ -CO	0.0112	17,900
C ₂ H ₂ -S	0.0905	2,210
S-C ₃ H ₄	0.0034	59,000
O ₂ -S	0.0178	11,200
C ₂ -HCl ³⁵	0.0233	8,580
C ₂ H ₄ -Ar	0.0689	2,900
C ₂ H ₇ -Br ⁷⁹	0.1365	1,470
C ₁₁ H ₁₂ -Hg ²⁰²	0.2022	990

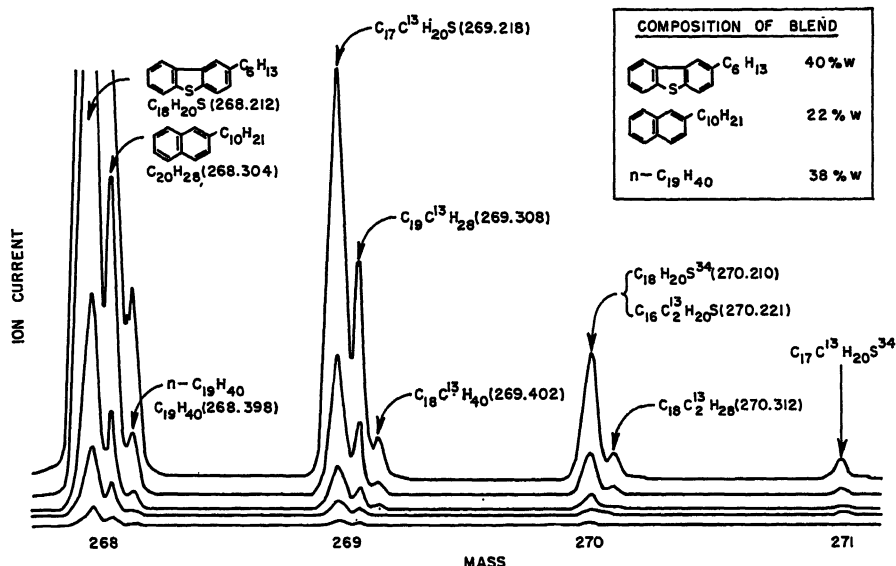


FIG. 8. High-resolution mass spectrum of a blend of pure compounds of nominal mass 268.¹⁶

shown in Table 3. The great variety arises from the presence of atoms other than carbon and hydrogen. Some of the important doublets not specifically given in this table can be calculated from the basic doublets. For instance, the mass difference for the $C_3H_5-CO_2$ doublet is twice the mass difference for the CH_4-O doublet. The resolution required at mass 200 is given in the last column of Table 3. A more extensive list of doublets commonly encountered in organic chemical work has recently been reported by Beynon.⁶

As an example of the usefulness of high-resolution techniques, the parent-peak region of a blend of 2-*n*-hexyldibenzothiophene, 2-*n*-decylnaphthalene, and *n*- C_{19} is shown in Figure 8 (reference 16). This spectrum was obtained on a double-focusing coincident-field mass spectrometer with a resolution of about 1 in 2000. Each of the three components of the blend has a nominal mass of 268, but the resolution of the mass spectrometer is sufficient to resolve the individual components, even though the mass separation is only 0.0905 amu between the thiophene and naphthalene and 0.0939 amu be-

tween the naphthalene and *n*-alkane. Peaks at masses 269, 270, and 271 are due to heavy isotopes, primarily those of carbon and sulfur.

The high-resolution mass-defect technique can be most useful in organic analysis, because it permits one to establish the particular combination of elements comprising a given mass peak. However, many elemental combinations (Table 3) require resolving powers even greater than those expected to be obtainable in analytical high-mass high-resolution mass spectrometers. Thus, the mass spectral approach to most identification problems must be made by a judicious combination of one or more methods based upon fragmentation patterns, isotopic abundance, and mass-defect identification.

REFERENCES

- ANDRÉ, M. L., HOOD, A., LONGMAN, R. T., AND O'NEAL, M. J., "Mass Spectrometric Analysis of High Boiling Aromatic Hydrocarbons," ASTM Committee E-14 Meeting, San Francisco, California, 1955.
- ANDRÉ, M. L., AND O'NEAL, M. J., *Anal. Chem.*, **31**, 164 (1959).
- ASSELINEAU, J., RYHAGE, R., AND STENHAGEN, E., *Acta. Chem. Scand.*, **11**, 196 (1957).

MASS SPECTROMETRY

4. BERGSTROM, H., RYHAGE, R., AND STENHAGEN, E., *Svensk. Papperstidning*, **60**, 96 (1957).
5. BEYNON, J. H., *Nature*, **174**, 735 (1954).
6. BEYNON, J. H., in J. D. Waldron, ed., "Advances in Mass Spectrometry," p. 328, Pergamon Press, London, 1959.
7. BREWER, A. K., AND DIBELER, V. H., *J. Res. NBS* **35**, 125 (1945).
8. BROWN, R. A., TAYLOR, R. C., MELPOLDER, F. W., AND YOUNG, W. S., *Anal. Chem.*, **20**, 5 (1948).
9. BROWN, R. A., *Anal. Chem.*, **23**, 430 (1951).
10. BROWN, R. A., MELPOLDER, F. W., AND YOUNG, W. S., *Petroleum Processing*, **7**, 204 (1952).
11. BROWN, R. A., YOUNG, W. S., AND NICOLAIDES, N., *Anal. Chem.*, **26**, 1653 (1954).
12. BROWN, R. A., SKAHAN, D. J., CIRILLO, V. A., AND MELPOLDER, F. W., *Anal. Chem.*, **31**, 1531 (1959).
13. BRUUN, H. H., RYHAGE, R., AND STENHAGEN, E., *Acta. Chem. Scand.*, **12**, 789 (1958).
14. CALDECOURT, V. J., *Anal. Chem.*, **27**, 1670 (1955).
15. CARLSON, E. G., AND O'NEAL, M. J., in "Symposium on Composition of Petroleum Oils," ASTM Special Technical Publication No. 224, p. 151, 1958.
16. CARLSON, E. G., HUNT, R. H., O'NEAL, M. J., AND PAULISSEN, G. T., "Adaptation of a Coincident Field Mass Spectrometer for the Study of High Molecular Weight Petroleum Fractions," ASTM Committee E-14 Meeting, Los Angeles, California, 1959.
17. CLERC, R. J., HOOD, A., AND O'NEAL, M. J., *Anal. Chem.*, **27**, 868 (1955).
18. CRABLE, G. F., AND COGGESHALL, N. D., *Anal. Chem.*, **30**, 310 (1958).
19. CRAIG, R. D., AND ERROCK, G. A., in J. D. Waldron, ed., "Advances in Mass Spectrometry," p. 66, Pergamon Press, London, 1959.
20. DINEEN, G. U., COOK, G. L., AND JENSEN, H. B., *Anal. Chem.*, **30**, 2026 (1958).
21. EDWARDS, R. T., *Ind. Eng. Chem.*, **47**, 2555 (1955).
22. EDWARDS, R. T., *Petrol. Refiner*, **36**, 180 (1957).
23. EVANS, E. D., KENNY, G. S., MEINSCHN, W. G., AND BRAT, E. E., *Anal. Chem.*, **29**, 1858 (1957).
24. FRIEDLAND, S. S., LANE, G. H., LONGMAN, R. T., TRAIN, K. E., AND O'NEAL, M. J., *Anal. Chem.*, **31**, 169 (1959).
25. GORDON, R. J., MOORE, R. J., AND MULLER, C. E., *Anal. Chem.*, **30**, 1221 (1958).
26. HALLGREN, B., STENHAGEN, E., AND RYHAGE, R., *Acta. Chem. Scand.*, **11**, 1064 (1957).
27. HASTINGS, S. H., JOHNSON, B. H., AND LUMPKIN, H. E., *Anal. Chem.*, **28**, 1243 (1956).
28. HASTINGS, S. H., JOHNSON, B. H., LUMPKIN, H. E., AND WILLIAMS, R. B., in "Symposium on Composition of Petroleum Oils," ASTM Special Technical Publication No. 224, p. 250, 1958.
29. HOOD, A., *Anal. Chem.*, **30**, 1218 (1958).
30. HOOD, A., AND O'NEAL, M. J., in J. D. Waldron, ed., "Advances in Mass Spectrometry," p. 175, Pergamon Press, London, 1959.
31. HOOD, A., CLERC, R. J., AND O'NEAL, M. J., *J. Inst. Petroleum*, **45**, 168 (1959).
32. KEARNS, G. L., MARONOWSKI, N. C., AND CRABLE, G. F., *Anal. Chem.*, **31**, 1646 (1959).
33. KING, W. H., MCSWEENEY, W. P., KANT, F. H., AND PRIESTLEY, W., "An Approach to Mass Spectrometer Analysis of High Molecular Weight Petroleum Fractions," ASTM Committee E-14 Meeting, San Francisco, California, 1955.
34. LUMPKIN, H. E., THOMAS, B. W., AND ELLIOTT, A., *Anal. Chem.*, **24**, 1389 (1952).
35. LUMPKIN, H. E., AND JOHNSON, B. H., *Anal. Chem.*, **26**, 1719 (1954).
36. LUMPKIN, H. E., *Anal. Chem.*, **28**, 1946 (1956).
37. LUMPKIN, H. E., *Anal. Chem.*, **30**, 321 (1958).
38. LUMPKIN, H. E., AND NICHOLSON, D. E., *Anal. Chem.*, **32**, 74 (1960).
39. MAYO, P. DE, AND REED, R. I., *Chem. and Ind.*, **1956**, 1481.
40. McLAFFERTY, F. W., *Anal. Chem.*, **28**, 306 (1956).
41. MEINSCHN, W. G., Preprints ACS Division of Petroleum Chemistry **3**, No. 4, C-51 (1958).
42. MELPOLDER, F. W., BROWN, R. A., WASHALL, T. W., DOHERTY, W., AND YOUNG, W. S., *Anal. Chem.*, **26**, 1904 (1954).
43. MELPOLDER, F. W., BROWN, R. A., WASHALL, T. A., DOHERTY, W., AND HEADINGTON, C. E., *Anal. Chem.*, **28**, 1936 (1956).
44. NILSSON, M., RYHAGE, R., AND VON SYDOW, E., *Acta. Chem. Scand.*, **11**, 634 (1957).
45. O'NEAL, M. J., AND WIER, T. P., *Anal. Chem.*, **23**, 830 (1951).
46. O'NEAL, M. J., U.S. Dept. of Commerce, Natl. Bur. Standards Circ. **522**, 217 (1953).
47. O'NEAL, M. J., in "Applied Mass Spectrometry," p. 27, Inst. Petroleum, London, 1954.
48. O'NEAL, M. J., HOOD, A., CLERC, R. J., ANDRÉ, M. L., AND HINES, C. K., Proc. Fourth World Petroleum Congress, Rome, Sec. V, p. 307, 1955.
49. O'NEAL, M. J., AND HOOD, A., Preprints ACS Division of Petroleum Chemistry **1**, No. 4, 127 (1956).

50. ORKIN, B. A., BENDORAITIS, J. G., BROWN, B., AND WILLIAMS, R. H., in "Symposium on Composition of Petroleum Oils," ASTM Special Technical Publication No. 224, p. 59, 1958.
51. OTVOS, J. W., AND STEVENSON, D. P., *J. Am. Chem. Soc.*, **78**, 546 (1956).
52. REED, R. I., *J. Chem. Soc.*, **1958**, 3432.
53. RYHAGE, R., STENHAGEN, E., AND VON SYDOW, E., *Acta. Chem. Scand.*, **10**, 158 (1956).
54. RYHAGE, R., STENHAGEN, E., AND VON SYDOW, E., *Acta. Chem. Scand.*, **11**, 180 (1957).
55. RYLANDER, P. N., MEYERSON, S., AND GRUBB, H. M., *J. Am. Chem. Soc.*, **79**, 842 (1957).
56. SAUER, R. W., MELPOLDER, F. W., AND BROWN, R. A., *Ind. Eng. Chem.*, **44**, 2606 (1952).
57. SCHISSLER, D. O., STEVENSON, D. P., MOORE, R. J., O'DONNELL, G. J., AND THORPE, R. E., "Steranes in Petroleum," ASTM Committee E-14 Meeting, New York, 1957.
58. SHARKEY, A. G., WOOD, G., AND FRIEDEL, R. A., *Chem. and Ind.*, **1958**, 833.
59. STEVENS, N. P., BRAY, E. E., AND EVANS, E. D., *Bull. Am. Assoc. Petroleum Geol.* **40**, 975 (1956).
60. THOMAS, B. W., AND SEYFRIED, W. D., *Anal. Chem.*, **21**, 1022 (1949).
61. TURNER, W. R., BROWN, D. S., AND HARRISON, D. V., *Ind. Eng. Chem.*, **47**, 1219 (1955).
62. VOORHIES, H. G., ROBINSON, C. F., HALL, L. G., BRUBAKER, W. M., AND BERRY, C. E., in J. D. Waldron, ed., "Advances in Mass Spectrometry," p. 44, Pergamon Press, London, 1959.
63. WASHBURN, H. W., WILEY, H. F., AND ROCK, S. M., *Ind. Eng. Chem., Anal. Ed.*, **15**, 541 (1943).
64. WASHBURN, H. W., WILEY, H. F., ROCK, S. M., AND BERRY, C. E., *Ind. Eng. Chem., Anal. Ed.*, **17**, 74 (1945).

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SURFACE IONIZATION METHOD

The surface ionization ion source for mass spectroscopy is a valuable technique for analyzing elements which cannot be easily combined into volatile chemical compounds and analyzed by conventional gas mass spectrometry. When material with ionization

potential I is deposited on a filament of work function W and heated in the source region of a mass spectrometer, there is a finite probability that some of the material will evaporate as positive ions according to the Kingdon-Langmuir law¹:

$$\frac{n^+}{n^0} = e \frac{F(W - I)}{RT}$$

where n^+/n^0 is the ratio of positively charged to neutral particles evaporated, F is the Faraday number, R is the gas constant, T is the absolute temperature and e is the Napierian base. M. G. Inghram and R. J. Hayden² report compounds of 54 elements which can be ionized by this technique. In addition to this list, valuable applications have been made on uranium and trans-uranium elements.

If the material to be analyzed has an ionization potential of about seven volts, the ionization efficiency from a tungsten or tantalum filament is rather low. This efficiency improves with increased temperature, but the sample volatilizes more rapidly. The operating temperature must be a compromise between efficiency of ionization and sample life. The use of multiple filaments in the source³ is a means of accomplishing this compromise. The sample is deposited on one of the filaments which is operated at a temperature sufficient to evaporate the sample at a controlled rate. Another filament in close proximity to the sample filament is operated at a higher temperature at which the efficiency of ionization is greater for those molecules which reach the hotter filament. The use of a multiple filament source and an electron multiplier for the detection of ions in a surface ionization mass spectrometer enables one to analyze fractional microgram quantities of many elements.

The introduction of solid samples to a mass spectrometer is more complicated than introduction of a gas sample. If the machine is opened to atmosphere while the sample filament is being installed, it may require

MASS SPECTROMETRY

several hours to pump down to operating pressure. Vacuum locks⁴ have been devised for introducing solid samples without excessive pressure increase in the spectrometer. The use of vacuum locks on single filament machines permits pump down to operating pressure within minutes after sample introduction.

Surface ionization mass spectrometry has an application in the isotopic studies related to geologic, cosmologic and geochronologic research. It is a particularly valuable technique where only minute quantities of low vapor pressure material are available.

An extensive application of surface ionization mass spectrometry is for the analysis of uranium isotopes. The recovery of uranium from spent reactor fuels requires isotopic and total uranium analysis of samples which vary widely in burn-up. The use of gas mass spectrometry on uranium converted to hexafluoride has disadvantages of memory effects and large (milligram quantities) sample requirements. The use of an isotope dilution method makes it possible to determine uranium concentration and uranium isotopic analysis on microgram quantities of highly radioactive samples. In brief, the method consists of adding a known amount of U^{238} isotope to a known volume of sample, mixing, semiquantitative separation of the uranium from the fission products and other diverse ions, and measurement of the relative abundance of the uranium isotopes with a surface ionization mass spectrometer. The memory effect with a single filament mass spectrometer is negligible because the entire sample filament is replaced when a new sample is introduced. That portion of sample which evaporates and condenses within the source region can give trouble.

Two manufacturers have announced plans to market mass spectrometers which can be used for surface ionization analysis:

Consolidated Electrodynamics Corp.
Pasadena
California

Nuclide Analysis Associates
State College
Pennsylvania

The Pennsylvania State University Mineral Industries Experiment Station Circular Number 55 is a compilation of abstracts for the years 1953-1956 relating to the mass spectroscopic analysis of solids.

REFERENCES

1. *Proc. Roy. Soc. A*, **107**, 61 (1925).
2. Nuclear Science Series Report Number 14 of National Academy of Sciences, National Research Council, 1954.
3. INGRAM, M. G., AND CHUPKA, W. A., *Rev. Sci. Instr.*, **24**, 518 (1953).
4. STEVENS, C. M., *Rev. Sci. Instr.*, **24**, 148-51 (1953).

THOMAS D. MORGAN

THEORY AND INSTRUMENTATION

Mass spectrometry deals with the separation of gaseous ions of differing mass and charge by the action of electrical and magnetic fields. By proper selection of experimental conditions, it is possible to measure precisely the mass of various ions, to prove existence of mass isotopes, and to measure relative abundance of ions in a mixture. Organic molecules produce, under proper conditions, a spectrum of ions corresponding to the parent molecule and most of the fragments which can be produced from it by bond rupture. Since mass spectra of even closely related organic molecules are quite different, mass spectrometry has become an important tool for analysis of organic mixtures in addition to its obvious utility in measuring isotope mass and abundance.

The mass spectrometer and the mass spectrograph, though based on the same principle, are quite different. The spectrograph is employed for precise measurement of mass while the spectrometer is designed to measure precisely relative abundance of ions. Both instruments are based on the observation of "positive rays" by Sir J. J. Thomson

in 1912. The first spectrometer was built by Dempster in 1918, while the first spectrograph was built by Aston a year later. In the following 25 years, the instruments were developed slowly and their application was confined primarily to university laboratories. Early in World War II, the need for precise, rapid analyses of complex hydrocarbon mixtures prompted development of several commercial spectrometers suited for this specialized application. Since 1945, these commercially available instruments have been developed into versatile tools for the analysis of a wide range of organic and inorganic compounds. This widespread application, has, in turn, prompted an extensive search for other means of mass discrimination and for simplified instruments suitable for process control application. Both have been successful, and a number of new, relatively simple instruments have appeared in the past 5 years.

In a mass spectrometer, the sample to be studied is first introduced into a vacuum bench, and, by suitable manipulation (including use of heat to vaporize solids and high-boiling liquids) reduced to a low vapor pressure. The vapor is then passed through a beam of electrons, where ionization occurs. All possible ionization reactions can and do occur, although the probability of some is much greater than others. The molecule as a whole may be ionized, or it may fragment in any possible manner, and the fragments in turn, may be ionized. Molecules or fragments can both add or lose one or more electrons, the loss of a single electron being the most common reaction. Ions thus produced are accelerated by a suitable electric field and passed into the magnetic field. A charged particle traveling at high speed follows a curved path, the radius of which depends on the speed of the particle and its mass-to-charge ratio (m/e). By varying either the speed of the particles (by changing the accelerating voltage) or by changing the magnetic field strength, ions of various m/e ratios

can be focused on a collector plate and thus grounded. The current flowing as a result is amplified and recorded by a suitable electrometer circuit. The resulting plot of mass versus ion intensity is known as a mass spectrum. It is reduced to a mass pattern by dividing each of the peak intensities by the intensity of the largest (or base) peak.

No two molecules behave exactly the same on electron bombardment. Even closely related molecules or isomers show some differences in the manner in which the various bonds react. Thus, mass spectra can be used for qualitative analysis. The problem of identification of pure compounds and some mixtures is simplified by the fact that most molecules give rise to some ions of the same mass as the parent molecule, and thus the absolute molecular weight can be established directly. In mixtures, it is not always possible to identify these "parent mass peaks," and other methods must be used. From the study of many mass spectra, an experienced spectrographer can form generalities in behavior which aid him in predicting the probable components in the sample. The final identification, as in most types of qualitative analysis, requires direct comparison of the spectra of the known and unknown.

In quantitative analysis, the problem is somewhat different. First of all, the qualitative analysis of the sample must be known or determined. The mass spectrum of a mixture is then simply the sum of the spectra of the components in the ratio of their partial pressures in the sample. The method of establishing the ratio of components depends on the components in the sample. In the simplest case, each component gives rise to a characteristic ion not formed by any other component, and a direct breakdown of the mixture is possible. In the other extreme, each component gives rise to some of each of the observed mass peaks, and linear simultaneous equations are needed to make the analysis. Consider the simple example of a mixture of *n*- and iso-butane. Here, both

MASS SPECTROMETRY

molecules have a 58 peak due to the parent molecule and a 43 peak due to the fragment remaining after the loss of a methyl group.

$$M_{58} = a_{58}x + b_{58}y$$

$$M_{43} = a_{43}x + b_{43}y$$

where M is the peak intensity, a and b the pattern coefficients measured for the pure components, and x and y the concentrations of *n*- and iso-butane, respectively. Solution of these equations leads to the analysis of the mixture. There is no limit, in theory, to the number of components which can be handled in this manner. In practice, it becomes difficult to find a mixture of more than 8 or 10 compounds which can be effectively handled. Electrical computers for the solution of 12 linear simultaneous equations are available to help in this work.

The analysis of most mixtures is done by combining these two approaches. Some compounds in the mixture give rise to characteristic peaks, and their contributions can be subtracted directly. Linear equations may then be set up to handle the remaining components. By suitable combinations of techniques, twenty or more components can be determined in a single mixture.

Mass spectrometric analyses are relatively rapid, an hour or two generally being sufficient for the analysis of a moderately complicated mixture. Where a sufficient number of samples of a given type are being analyzed, specialized computational facilities may be used to reduce this time considerably. In the extreme case, the signal from the electrometer circuit is fed directly into an electrical computer (rather than a recorder) and the calculation made directly. In this case, the answer is available almost as soon as the spectral scan has been completed.

The precision and accuracy of the instrument likewise depend on the type of sample being examined. In general, ± 1 mole per cent can be achieved.

The mass spectrometer has been success-

fully applied to the analysis of many different and difficult samples. Its most remarkable successes have come in the field of petroleum hydrocarbons, where the similarity of structure and the chemical inertness of the compounds had made precise, rapid analyses by other techniques difficult, if not impossible.

The mass spectrometer can be applied to many other types of analyses. At least two commercial instruments are available for the precise measurement of ratios of peak intensities. This equipment is used for following the presence of such tracer elements as C^{13} and N^{15} , and thus plays an important role in medical and biological research. The success of the mass spectrometer in the field of analysis of volatile components has prompted the search for a source suitable for the ionization of metals. This has been done, although the technique is difficult. Instruments specially designed for monitoring process streams have also been developed.

R. E. KITSON

TIME-OF-FLIGHT SPECTROMETRY

Comparison with Other Mass Spectrometers

Many different types of mass spectrometers have been developed over the past sixty years. To help explain the differences between the Bendix Mass Spectrometer and others, a brief review of the operating principles of several kinds of spectrometers will be given.

Magnetic Deflection Mass Spectrometer. One of the commonest types of mass spectrometers operates on the magnetic deflection principle. Here separation according to mass to charge ratio occurs when a beam of nearly mono-energetic ions enters a magnetic field which is at right angles to the velocity of the ion. A continuous beam of ions is used, and the spectrum is scanned by varying either the ion accelerating voltage

or the strength of the magnetic field. Varying either of these parameters causes each of the separated m/e ion beams to pass in turn across a fixed slit in front of a collector, the signals of which are amplified and fed to a recorder. A simultaneous record of all peaks may be taken by allowing the mass separated and focused ion beam to develop a photographic plate.

Cycloidal Focusing Mass Spectrometer. Crossed electric and magnetic fields are utilized by the cycloidal focusing mass spectrometer (Fig. 1). After initial acceleration in the source, the ion beam enters the crossed field region which causes all ions to follow prolate cycloidal paths. The spectrum passes by the fixed collector slit as either of the two crossed fields is varied. This spectrometer was first proposed by Bleakney and Hipple in 1938¹ and has since been further developed^{2, 3} and made commercially available by Consolidated Electrodynamics Corporation.^{4, 5}

R.F. Mass Spectrometer. Mass separation in electric fields alternating at radio frequencies is realized in several spectrometers. One of these is the Bennett Tube (Fig. 2) invented by Dr. Willard H. Bennett and first reported by him in 1950.⁶ Other papers on this instrument have since appeared.⁷⁻¹² After all ions are accelerated to the same energy, they enter one or more radio frequency stages where out-of-phase ions lose energy and resonant ions gain energy (the RF grid changes polarity relative to the adjacent grids just as the resonant ion passes through it). The retarding potential applied to the anode repels all ions except those possessing maximum energy. The ion beam is accelerated continuously, and the mass spectrum is scanned by varying the frequency of the alternating voltage.

Walt Donner, while at Beckman Instruments in California, developed another RF spectrometer^{13, 14} (Fig. 3). The Beckman Mass Spectrometer is quite similar to the Bennett Tube, although the final energy selection is done by deflecting the ions rather

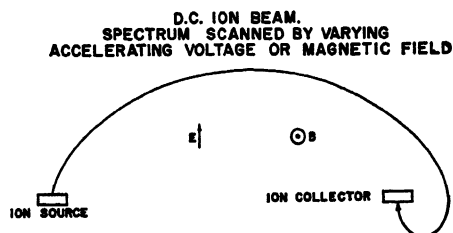


FIG. 1. Schematic of cycloidal focusing mass spectrometer.

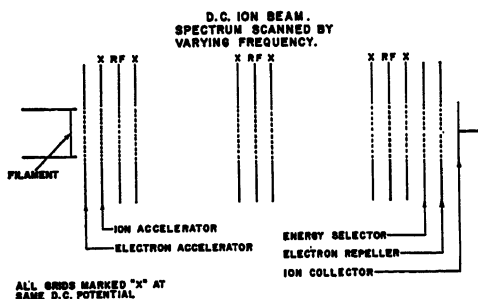


FIG. 2. Schematic of Bennett Tube.

than by repelling them. Again the ion beam is continuous, and mass scanning is done by varying frequency.

Omegatron. The Omegatron (Fig. 4), invented by Hipple, Sommer, and Thomas,¹⁵⁻²⁰ uses crossed magnetic and RF electric fields. Its operation is very similar to that of a cyclotron, except in the Omegatron the electric field is essentially uniform throughout the ion path region, whereas the cyclotron electric field exists only between the two dees. As in the two RF instruments described above, ion resonance is used here for mass selection. Ions whose frequency of rotation coincides with the frequency of the electric field travel in an ever expanding spiral, eventually hitting the collector. The ion beam is continuous, and the electric field frequency is varied to scan the mass spectrum.

Magnetic Time-of-Flight Mass Spectrometer. Dr. Goudsmit, Chairman of the Physics Department at Brookhaven National Laboratory, developed a magnetic time-of-flight spectrometer (Fig. 5) in which

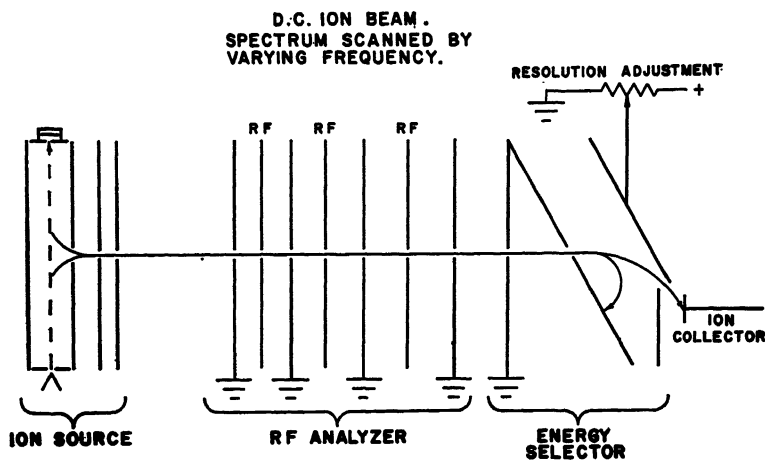


Fig. 3. Schematic of Beckman RF Mass Spectrometer.

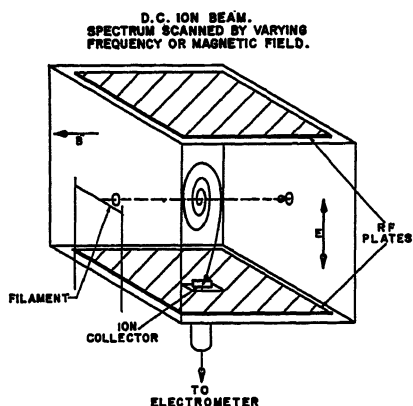


Fig. 4. Schematic of Omegatron.

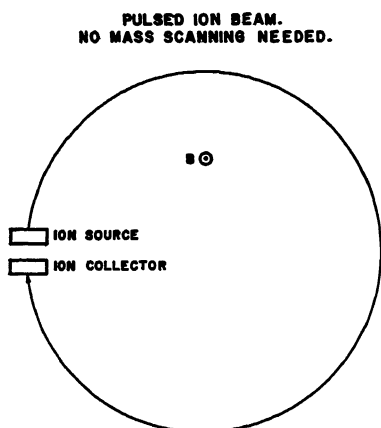


Fig. 5. Schematic of magnetic time-of-flight mass spectrometer.

ions are allowed to complete 360 degrees of rotation in a uniform magnetic field.²¹ An early version of his instrument operates at a repetition frequency of 300 cps, and the ion beam is pulsed. The electric field which accelerates the ions out of the ion source drops to zero before any but the lightest ions emerge, so that all heavier ions receive equal momenta and therefore follow the same path in the magnetic field. As the ions complete a full circle, they automatically focus to form an image of their original space distribution in the ion source, so both space focusing and mass separation are inherent in Dr. Goudsmit's device. His instrument is capable of a resolution of one part in 1000 at all masses. Since no mass scanning is used, the ion signal amplifier needs a wide band width to avoid widening the individual ion peaks and thereby hurting resolution. For that reason, an electron multiplier²² was chosen as the ion signal detector and amplifier. The output of this multiplier is displayed on an oscilloscope which is synchronized with the spectrometer frequency.

Non-Magnetic Time-of-Flight Mass Spectrometers. Fig. 6 shows the essential features of a non-magnetic TOF mass spectrometer. Here, both the electron beam and the ion beam are pulsed, and all ions receive

the same energy. (More correctly, all ions with the same charge receive the same energy. In the following discussion, only singly charged ions will be considered.) The ion bunch created at the beginning of each cycle is accelerated into the field free drift space between the source and detector. Since these ions have a mass dependent velocity, the lightest ions reach the detector first followed in succession by ions of heavier mass. No mass scanning is ordinarily used, so again an ion detector of wide bandwidth is needed.

Cameron and Eggers reported the first working non-magnetic TOF mass spectrometer in 1948.²³ Their spectrometer contains a ten foot drift space between the single grid ion source and the detector, and all ions are accelerated through 300 volts. The resolution of their first experimental device was poor, but their work encouraged others to investigate time-of-flight spectrometry more thoroughly.

Another TOF mass spectrometer, similar to the one built by Cameron and Eggers, was reported by Wolff and Stephens in 1953.²⁴ Their one grid ion source accelerates all ions to 250 volts, and the ion flight path between source and detector is 100 cm. long. Discernible adjacent mass separation extends to about mass 12.

In April of 1955, Katzenstein and Friedland reported²⁵ their TOF mass spectrometer in which the electron beam is parallel to the direction of ion acceleration as in the Bennett Tube. Several electric fields are used in the ion source region, and the ions possess an energy of 250 volts during their 100 cm. flight to the collector. A grid near the collector is excited once each cycle by a 0.1 microsecond negative pulse (the ion selector pulse). Only the ions gaining this extra energy can pass the repeller grid placed just before the collector. The mass spectrum is scanned, thus eliminating the wide bandwidth requirements on their amplifier, by slowly changing the time delay between the ion accelerating pulse in the ion source and

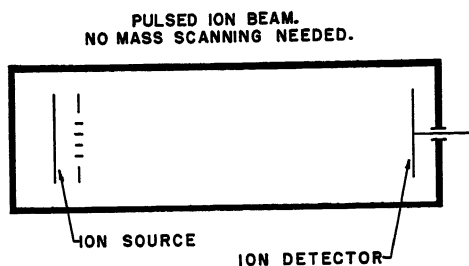


FIG. 6. Schematic of non-magnetic time-of-flight mass spectrometer.

the 0.1 microsecond ion selector pulse. Their paper reported useful adjacent mass resolution beyond mass 75.

Bendix Time-of-Flight Mass Spectrometer

Bendix Aviation Corporation sponsored the development of a non-magnetic time-of-flight mass spectrometer first reported by Wiley and McLaren in December of 1955.²⁶ Other papers on this instrument have since appeared.²⁷⁻³⁰ The Wiley-McLaren paper shows how the experimental resolution (greater than any non-magnetic mass spectrometer) agrees closely with mathematical theory. The high resolution is due to the invention, by W. C. Wiley, of a new two grid ion source based on a careful mathematical study of the focusing properties of all types of time-of-flight mass spectrometers. Bendix continued to develop their spectrometer, and in 1957 they made it commercially available. Fig. 7 is a schematic of this instrument.

Operation. The Bendix Mass Spectrometer operates at a repetition frequency of 10,000 cycles per second, and therefore produces 10,000 complete mass spectra each second. The first event in each cycle is the creation of the ionizing electron beam. The electrons are generated from an internally heated .005 inch diameter tungsten wire and are normally kept from entering the ionization region by a negative bias on the control grid. At the beginning of each cycle, a .25 microsecond positive pulse is applied to the control grid, allowing the magnetically col-

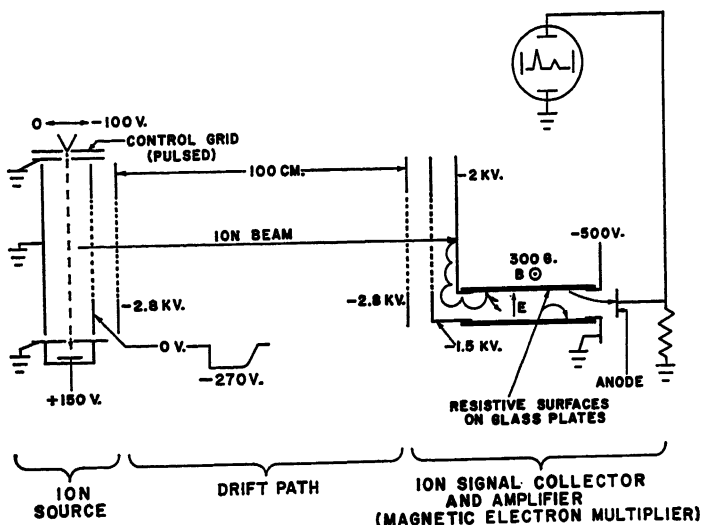


Fig. 7. Schematic of Bendix Time-of-Flight Mass Spectrometer.

limited electron beam to pass through the ionization region. The energy of the electron beam is determined by the difference between the D.C. potential on the filament and the ground potential on the second grid of the electron gun. Therefore, the filament potential determines the electron energy, which is variable between 0 and 100 volts. During ionization, all elements surrounding the ionization chamber are at ground potential. Immediately after the electron beam is turned off, the first grid in the ion gun is pulsed to about -270 volts, and this pulse remains long enough (2.5 microseconds) for all ions of interest to pass through this grid into the accelerating region of the source. Here they are accelerated by a 2800 volt potential on the ion energy grid. This final grid in the ion gun is about 1.6 centimeters away from the electron beam, and the ion detector is about 100 centimeters further down the tube. These parameter values give a time of flight in microseconds which is roughly equal to the square root of $2m/e$, where m is the mass of the ion in atomic mass units and e is the ion's charge in electron charges. Mass separation results only from the mass dependent velocities; no electric or

magnetic fields are used to enhance separation.

If the ions before pulsing were at rest and all in a plane parallel to the electrodes, almost any method of ejecting them from the source would provide infinite mass resolution, regardless of the total length of the flight path. The resolving power of the instrument is, therefore, a measure of the ability of the source to deliver the ions of one mass to charge ratio to the detector in a sharp pulse, even though the ions will inevitably vary in initial position and velocity. The effect of variations in the initial position of the ion can be reduced by taking advantage of the fact that those ions farther away from the -270 v. grid fall through a larger potential during the ion-ejection period than do those nearer this grid. The trailing ions will, therefore, acquire a greater velocity and will eventually overtake those in front. A proper adjustment of the fields in the ionizing and accelerating regions, made by varying the height of the ion-ejecting pulse, causes the "crossover point" for all ion peaks to occur as they pass into the ion signal detector (electron multiplier). The harmful effect of initial ion velocities

on the resolution of a time-of-flight spectrometer can be reduced in two ways: 1) the final velocity of the ions can be made large relative to their initial velocities; 2) the time during which the ions are traveling with their final velocities can be made large compared with the total time of flight. The latter method has the effect of increasing the average velocity of the ions during their total flight time relative to their initial velocities. The high resolution produced by the Bendix spectrometer compared with other time-of-flight instruments is in large measure due to its ability to give the ions a high average velocity without using prohibitively high voltages or requiring a speed of response in the ion detector and output system beyond present electronic art.

A mathematical treatment of the focusing action of this spectrometer can be found in the article by Wiley and McLaren.²⁶

Magnetic Electron Multiplier. A magnetic electron multiplier, which operates in crossed electric and magnetic fields, was chosen as the ion signal detector and amplifier for four reasons:

(1) It permits the use of a plane ion cathode which eliminates the ion transit time variations encountered with the curved ion cathode of the conventional electrostatic multiplier.

(2) Only this type of multiplier provides the necessary bandwidth conveniently. Each mass signal is less than 50 millimicroseconds wide at its base, and a bandwidth considerably above 20 megacycles is needed to preserve this pulse shape.

(3) The extremely wide bandwidth of this multiplier (D.C. to 500 megacycles) permits many stages of multiplication to be used without influencing resolution, thereby permitting a low gain per stage. This, in turn, allows the use of chemically stable multiplying surfaces which can be exposed to air and washed without affecting the secondary emission ratio.

(4) It is possible to switch the electron

beam inside the multiplier from one anode to another very swiftly. Switching times between 5 and 10 millimicroseconds are common, permitting effective isolation of signals corresponding to particular masses.

Wiley devised a new design for this multiplier involving two pieces of resistive glass, each about $5 \times 1\frac{1}{4} \times \frac{1}{4}$ inches. The resistive coating is thin but very tenacious, both chemically and physically, permitting conventional chemical cleaning as well as non-gritty abrasive cleaning (pencil eraser, finger nail or Bon-Ami). Exposure to wet air has no observable effect on multiplying power.

Oscilloscope Output. The voltage waveform (mass spectrum) produced by the multiplier is displayed on an oscilloscope synchronized with and triggered by the mass spectrometer. Any portion of the mass spectrum can be viewed in any desired detail by adjusting the horizontal sweep speed controls on the oscilloscope and the continuously variable delay on the spectrometer between the ion accelerating pulse and the oscilloscope trigger.

Resolution. Figure 8 shows the mass spectrum of xenon displayed on an oscilloscope which illustrates the resolution attainable with this instrument.

Other resolution measurements show that the oscilloscope trace between mass 200 and 201 reaches the baseline, that there is a 10 % peak height interference between equal peaks at mass 422 and 423, and that the theoretical half height width of mass 600 is equal to the adjacent mass separation. The mass range of the spectrometer extends from 0 to about 5000 a.m.u., since the time-of-flight of mass 5000 is about 100 microseconds, the spectrometer's period. If ions having a mass of 6000 a.m.u., for instance, were created during one cycle, they would arrive at the multiplier during the next succeeding cycle, producing overlapping spectra. Such heavy ions are difficult to produce in a mass spectrometer, however, and the practical mass range



Fig. 8. Oscilloscope presentation of xenon spectrum obtained with Bendix Time-of-Flight Mass Spectrometer. Masses, from left to right, 128, 129, 130, 131, 132, 134 and 136 a.m.v.

of the Bendix Mass Spectrometer can be said to be unlimited.

Sensitivity. Until recently, the absolute sensitivity of the commercial version of the Bendix Mass Spectrometer had been such that an argon partial pressure of about 2×10^{-8} mm Hg in the ionization region produced, on the average, about one detected argon ion at the output each cycle, or 10,000 ions per second. Design and operating changes in the electron gun have recently become available which increase absolute sensitivity up to 30 times. There are (1) a 4-fold increase in the cross sectional area of the electron beam (with a resulting 15 % reduction in resolution), (2) operation of the electron gun near saturation, and (3) a 5-fold increase in the time duration of the control grid pulse (the positive going pulse that gates-on the electron beam). These changes give an absolute sensitivity of the commercial instrument such that one detected argon ion at the output each cycle, or 10,000 ions each second, are produced for an argon partial pressure in the ion source of about 7×10^{-10} mm Hg.

The relative sensitivity of this instrument is such that 5 parts per million of tin has been seen in a sample evaporated in a vacuum furnace, and also 2.5 ppm of phenyl ethyl chloride in phenyl ethyl alcohol. The theoretical limit on relative sensitivity in a mass spectrometer is given by the difference

between the largest ion signal that can be detected compared to the noise in the output system. The Bendix mass spectrometer, equipped with the electron gun modifications listed above, can produce an ion peak at mass 28 which contains upwards of 1000 ions each cycle. The limiting noise in the output system is given by the electron multiplier, which produces about one ion-type noise pulse every 100 seconds, or one ion-type pulse every one million cycles. This corresponds to an argon partial pressure in the ion source of 7×10^{-10} mm Hg. This theoretical relative sensitivity of 10^{10} is reduced in practice by the residual atmosphere in the vacuum system.

Recording Output System. The accuracy of the time-of-flight mass spectrometer was improved considerably by the development of a recording output system by Bendix in 1958. The key element in this recording output system is a new version of the Wiley Electron Multiplier utilizing its fast beam switching ability. A common version of this multiplier is shown schematically in Figure 9.

The electron beam within the multiplier ordinarily collects on the oscilloscope anode, but when a gating pulse is applied to either G1 or G2, the beam is collected on the corresponding anode for the duration of the gating pulse. This is ordinarily no longer each cycle than the duration of one mass signal

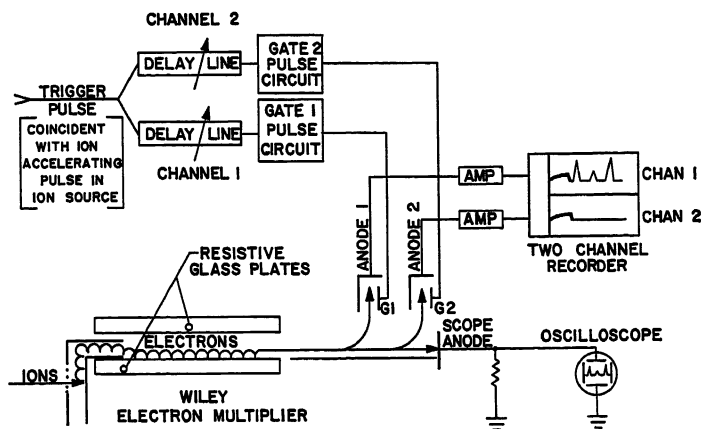


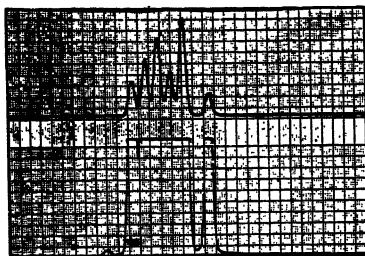
FIG. 9. Schematic of recording output system for Bendix Time-of-Flight Mass Spectrometer.

(about .05 microsecond). Mass peaks are selected by choosing appropriate values of delay on each channel. If these delays remain constant, a mass ratio of two peaks is recorded. If the delay of one channel (the "scanner" channel) changes steadily at a rate, for instance, of one mass decade every 15 seconds, that channel records a mass spectrum which is continuously compared with the peak selected by the other channel (the "controller" channel). The output from the controller channel can be fed back negatively to the multiplier gain control in such a way as to maintain that output at a constant value. This means the scanner channel's output is continuously compared to a constant value, permitting the use of a single channel recorder while preserving the advantage of a ratio output. This advantage is that changes in any spectrometer variable which affect all mass peaks proportionally, such as ion source pressure, have virtually no effect on peak ratios.

Recorded Spectra. Figure 10 shows the mercury spectrum produced by this recording output system. The voltage signal from only one gated multiplier anode was fed to both amplifiers of the two channel recorder. These amplifiers were adjusted to give a factor of ten gain difference between them, producing the two channel presentation of

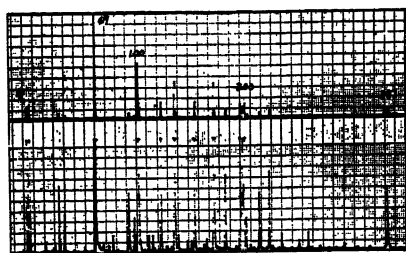
mercury. The resolution displayed by the recording is not as good as that shown on the oscilloscope since the voltage gate in the electron multiplier has a finite width. Figures 11 through 15 show various portions of the mass spectrum of Minnesota Mining and Manufacturing Compound FC-75. In common with most halogens, the parent peak, mass 416, is missing in this positive ion spectrum. The prominent peak at mass 397 results from one fluorine atom being broken away from the parent molecule during ionization. This $C_2F_{10}O$ compound is an excellent mass marker for mass identification work, since it not only has many known masses out to 397 atomic mass units, but it is also easily introduced into the mass spectrometer and easily pumped away after introduction. Its viscosity and appearance are very similar to those of water at room temperature (fortunately, it can be pumped out of a vacuum system more easily than water), and it boils at about 150 degrees centigrade under standard temperature and pressure.

Other Developments. In addition to the recording output system described above, Bendix has developed their original time-of-flight mass spectrometer in other directions. These developments may be divided into three groups: Sample inlets, vacuum sys-



Bendix

FIG. 10. Mercury isotopes as scanned on Bendix Time-of-Flight Mass Spectrometer. Masses, from left to right, 196, 198, 199, 200, 201, 202 and 204 a.m.u.

 C_2F_{10} MASS 31 TO 387

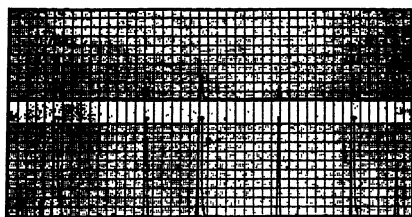
Bendix

FIG. 11

 C_2F_{10} MASS 31 TO 387

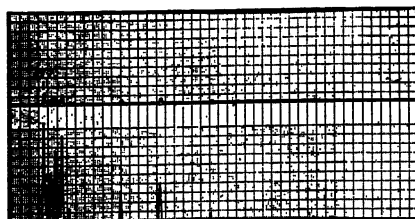
Bendix

FIG. 12

 C_2F_{10} MASS 33 TO 105

Bendix

FIG. 13

 C_2F_{10} MASS 100 TO 300

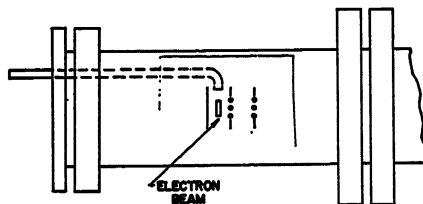
Bendix

FIG. 14

 C_2F_{10} MASS 300 TO 400

Bendix

FIG. 15



Bendix Mass Spectrometer, Cincinnati Div., The Bendix Corp.

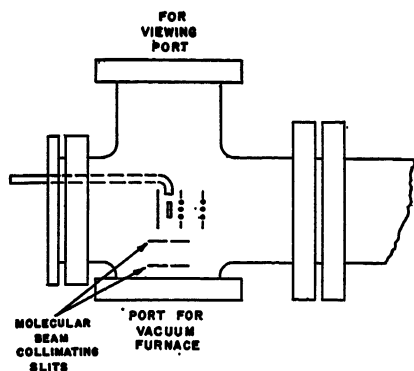
FIG. 16. Sample inlet systems. Sample inlet tube.

tems, and ion source operation. Each of these areas will be discussed in turn.

Sample Inlets

Sample Pipe Inlet—Molecular Beam Inlet System. The simplest and most straight forward way of introducing a sample into a mass spectrometer is through a small pipe or tube which passes through the vacuum wall of the spectrometer to the ionization region of the ion source. Fig. 16 pictures the $\frac{3}{16}$ -inch diameter stainless steel tube used to introduce samples which have sufficiently high vapor pressures. A molecular leak inlet system has been developed for this sample pipe inlet.

Molecular Beam Inlet. One of the two line-of-sight inlets is shown in Fig. 17. One important use for this inlet is the analysis of molecular beams, such as those produced by evaporating solids inside the vacuum system



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FIG. 17. Sample inlet systems: molecular beam inlet plus inlet tube.

of the mass spectrometer. This sample introduction method is needed to analyze materials having vapor pressures too low for gas handling systems. Another use for this line-of-sight inlet is the introduction of other ionizing beams such as a light beam from a vacuum monochromator.

Hot Filament Inlet System. Two methods have been developed for introducing and vaporizing solids, one of which is the hot filament sample inlet system, Fig. 18. This system consists primarily of a tantalum ribbon filament attached by screw clamps and insulated standoffs to the end of a smooth piston which operates through a vacuum lock arrangement. The sample to be analyzed is placed on the trough shaped filament, the piston is introduced into the spectrometer through the vacuum lock which is fastened to the bottom port shown in Fig.

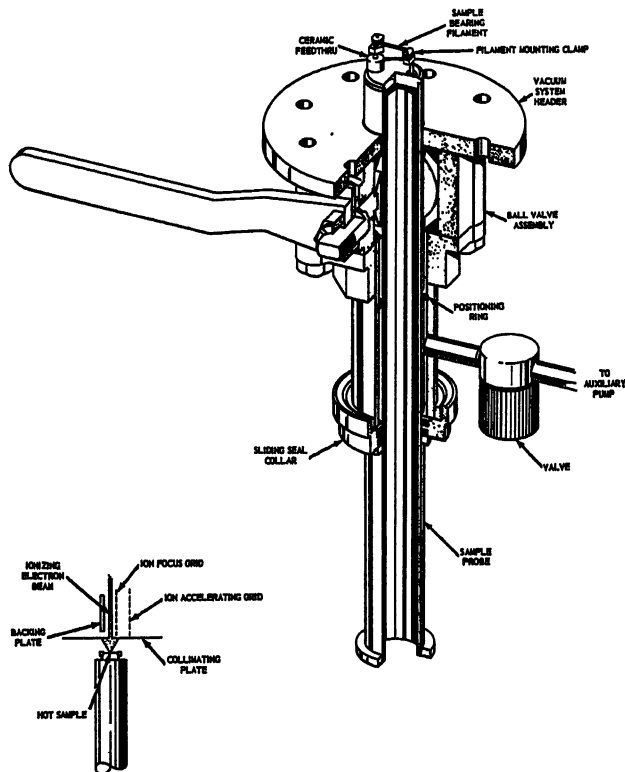


FIG. 18. The Bendix hot-filament inlet system, Model B-106.

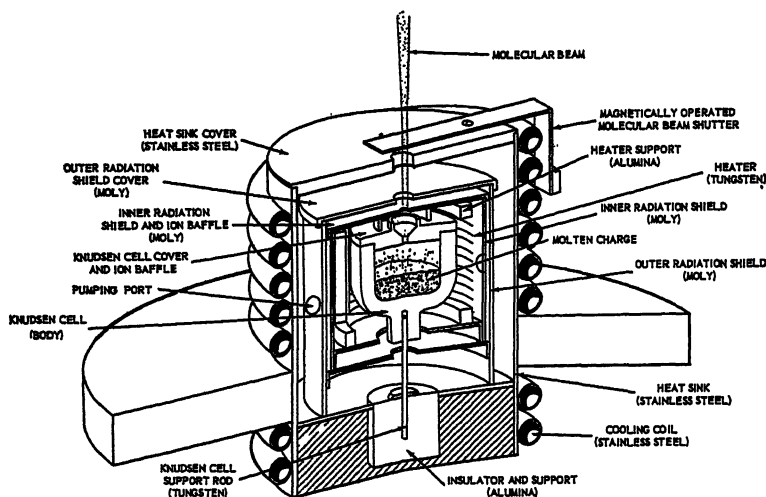


Fig. 19. Knudsen cell sample system for the Bendix Time-of-Flight Mass Spectrometer.

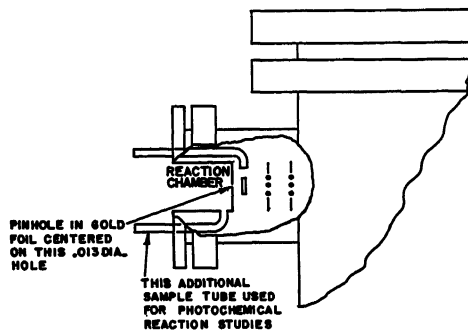
17, and the filament is heated by applying a variable voltage across it. The resulting vapor is then collimated so it will pass through the ion source without hitting any ion source elements, thereby keeping the source as clean as possible.

A new filament is ordinarily used for each sample, and these filaments are enough identical to permit one temperature calibration to serve for all. As long as the temperature of these filaments is kept below 500°C their temperature can be determined to within 25 degrees by measuring the applied current. In addition to analyzing low vapor pressure materials, this hot filament sample inlet system can be used for other applications such as molecular weight determinations and thermal degradation studies.

Knudsen Cell Inlet System. Another sample system for analyzing solids which has been developed for the Bendix Time-of-Flight Mass Spectrometer is patterned after the Knudsen cell, which is a crucible entirely enclosed except for a small hole through the top. This permits equilibrium to exist between the solid charge and its vapor. When used as a sample inlet system (see Fig. 19), the Knudsen cell is inserted into the spectrometer vacuum system

through the bottom port of Fig. 17 and is heated by electron bombardment to temperatures up to and above 2200 degrees centigrade. The collimating slits prevent the emitted vapor from hitting and dirtying ion source elements. This Knudsen cell sample system can be used for the same applications as the hot filament sample system described above, as well as for vapor pressure *vs.* temperature studies and investigations of vapors which are in equilibrium with their solids. One study using a Knudsen cell sample system will be described later in this article.

Pinhole Inlet. Fig. 20 shows the pinhole



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Fig. 20. Sample inlet systems: fast reaction pinhole inlet plus inlet tube.

inlet system designed especially for the study of fast reactions occurring at pressures below atmospheric. Fast reaction studies are made possible because 10,000 complete mass spectra are created each second, and because the ions for each spectra are created in $\frac{1}{4}$ microsecond. The pinhole inlet is situated immediately behind the ionizing electron beam so that intermediate reaction products can be ionized as soon after their creation as possible, and also so that ionization can take place where the sample stream pressure is still relatively high. A pinhole inlet whose diameter is no smaller than the thickness of the gold foil assures that a minimum of the particles passing through the pinhole will suffer wall collisions. Such wall collisions are undesirable because the particles analyzed in such work are ordinarily highly reactive.

For flash photolysis studies, the reaction chamber can be capped by a suitable window through which the light beam can pass. In this case, the reactant gas is introduced to the reaction chamber through the bottom tube. Analyses of shock waves inside a shock tube can be made with this inlet by building the shock tube in such a way that the reaction chamber is an extension of the shock tube itself. With such an arrangement, the pinhole inlet samples the center of the shock wave, and the disturbing effects caused by the shock tube walls are largely eliminated.

When the pressure of the fast reaction to be analyzed is over atmospheric, a differentially pumped inlet system is required. The purpose of such a system is to reduce the pressure of the incoming sample stream to molecular beam proportions as quickly as possible. Such a differentially pumped inlet system can be attached to either of the line-of-sight inlets shown in Figs. 17 and 20, but the molecular beam inlet (Fig. 17) is the more common choice. When used for differential pumping (and also for photoionization using a vacuum monochromator), the axis of the side ports is usually made horizontal rather than vertical as Fig. 17 shows.

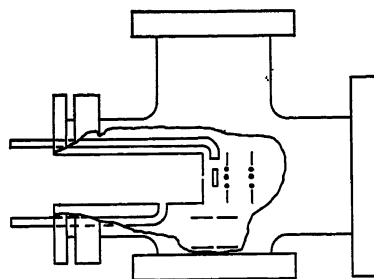
Three Inlets Combined. The open geometry permitted by the time-of-flight principle allows all three sample inlet systems to be combined into one instrument, as shown in Fig. 21.

Vacuum Systems

Smaller Vacuum System. Fig. 22 illustrates the smaller of the two vacuum systems developed for this instrument. The length of the horizontal tube is determined by the 100-cm. flight path between ion source and electron multiplier. Mercury diffusion pumps have been chosen for all standard models of the time-of-flight mass spectrometer to avoid the extensive background spectrum given by oil pumps.

Fast Reaction Vacuum System. The vacuum system designed expressly for fast reaction work and the pinhole inlet (Fig. 20) is shown in Fig. 23. The original design for this vacuum system was made by G. B. Kistiakowsky for a mass spectrometer built by him and by P. H. Kydd which operates on the Bendix time-of-flight principle. His instrument has been used for flash photolysis studies as well as for the analysis of shock tube waves, as described later.

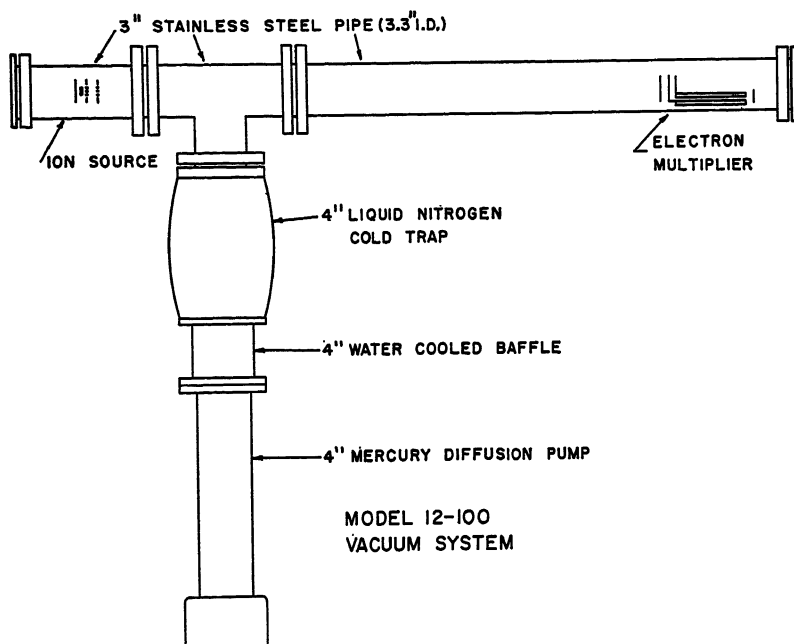
There are several requirements that must be fulfilled for satisfactory mass spectrometric analysis of fast reactions. These requirements stem from the highly reactive character of the particles being analyzed.



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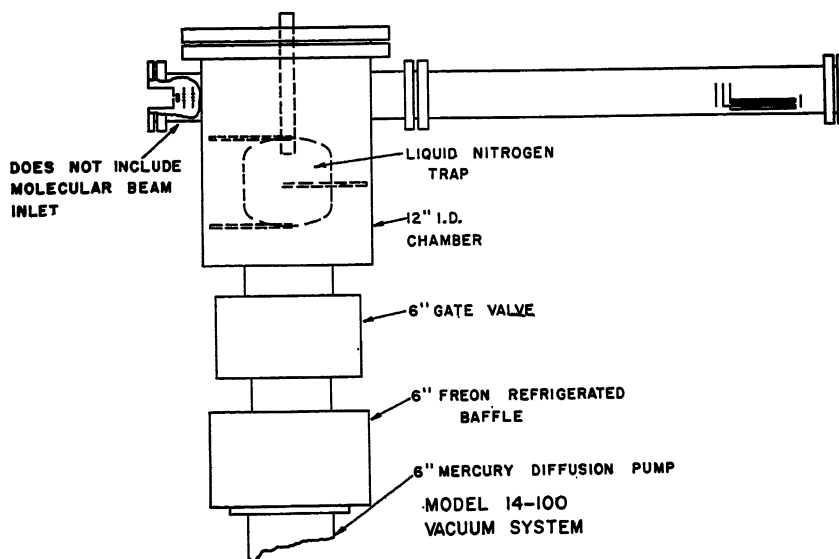
FIG. 21. Sample inlet systems: fast reaction pinhole inlet, plus molecular beam inlet, plus sample inlet tube.

MASS SPECTROMETRY



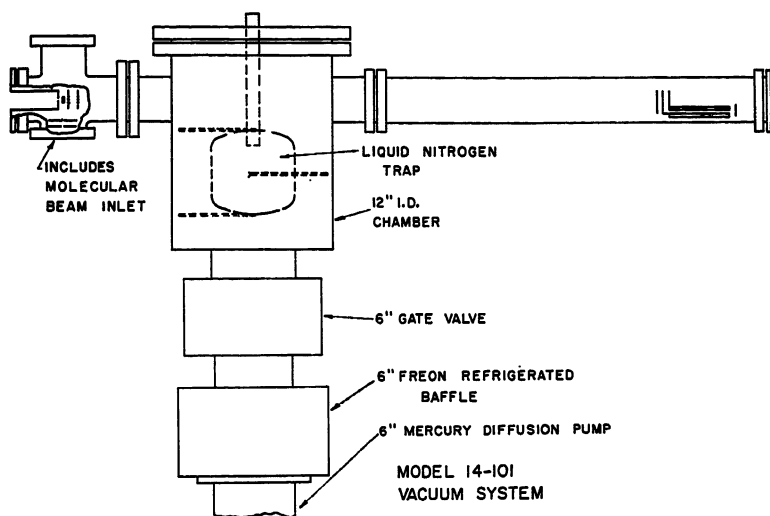
Bendix Mass Spectrometer, Cincinnati Div., The Bendix Corp.

FIG. 22



Bendix Mass Spectrometer, Cincinnati Div., The Bendix Corp.

FIG. 23



Bendix Mass Spectrometer, Cincinnati Div., The Bendix Corp.

FIG. 24

First, the sample must be introduced in a fashion to minimize wall collisions, and there must be a minimum number of collisions between particles before ionization. The pinhole inlet described above is an attempt to satisfy these needs. Another requirement is low background. Background gas in this case includes not only products from the diffusion pump and gases originating in the walls of the vessel, but also any molecules which have gone through the sample inlet and have rebounded against a surface at least once. To achieve these requirements, a large, fast, and well trapped diffusion pump is used plus a large evacuated region immediately beyond the ion source. In addition, the all stainless steel high vacuum region uses aluminum³¹ and gold gaskets throughout, so standard bakeout techniques can be used. The purpose of this design is not only to reduce background gases originating in the pump and the walls, but also to insure that the great majority of particles passing through the ion source the first time will be lost to the pump rather than return to the source.

Fig. 24 indicates the form taken by the Model 14 vacuum system when all three sample inlet systems are present.

Ion Source Operation

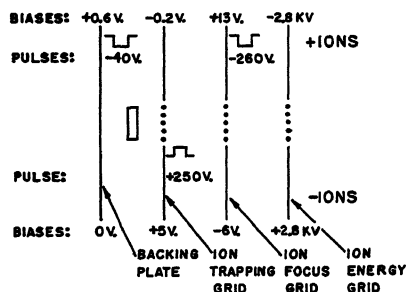
Pulsed—Positive and Negative Ions.

The first ion source designed for the Bendix Time-of-Flight Mass Spectrometer is shown in Fig. 7. Ions are produced by a pulsed electron beam, and immediately after their creation, the positive ions are accelerated out of the ion source by means of the negative going voltage pulse applied to the first grid. This two grid ion source can also accelerate negative ions into the drift path for analysis. For this, positive biases are applied to the ion gun and the negative going voltage pulse is applied to the backing plate.

Ion Trapping—Positive and Negative Ions. The three grid ion gun shown in Figure 25 makes it possible to analyze ions created by continuous ionizing beams or ions created outside the mass spectrometer. The voltage pulses are applied to the grids once every 100 microseconds; at other times the indicated biases are present. Consider a positive ion which has been introduced into the ion source as part of a sample. Since the trapping grid is more negative than either the focus grid or the backing plate, the positive ion will oscillate back and forth through the

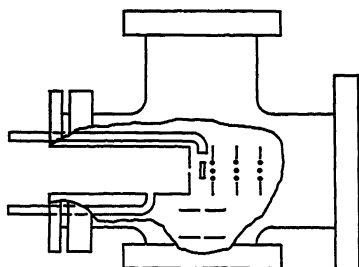
trapping grid until it either loses its charge to the grid, or until the negative going voltage pulses are applied to the source. When the pulses are applied, the positive ions to the right of the trapping grid are accelerated out of the source and are analyzed in the usual way. However, the positive ions to the left of this grid are accelerated to the backing plate and are lost. Also, any positive ions introduced to the ion source while the voltage pulses are being applied are also lost on the backing plate. As Fig. 25 shows, negative ions as well as positive ions can be analyzed in this fashion.

A continuous electron beam is provided for this mode of operation, but its use is generally limited to setting the spectrometer up for the particular experiment being run.



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Fig. 25. Ion source for analyzing either + or - ions created either inside or outside the mass spectrometer.



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Fig. 26. Ion source S-14-107 combines: 1. Sample inlet tube; 2. Molecular beam inlet; 3. Fast reaction pinhole inlet with the ability to analyze: a. Either + or - ions; b. Ions created either inside or outside the mass spectrometer.

If electron beam ionization can be used, there is no point in operating the source in the trapping grid fashion. This three grid operation reduces resolution by about 10%. There are three variable biases to contend with (although these are not sensitive in their adjustment), and the sensitivity of the instrument is not materially improved. For these reasons, Bendix has made it possible for any of their three grid ion sources to run in the two grid, pulsed electron beam fashion by providing external switches and plugs which convert the source in the following manner: the ion energy grid and ion focus grid are both connected to the 2.8 kilovolt ion energy potential, a single negative going voltage pulse is delivered either to the ion trapping grid or the backing plate depending upon the polarity of the ions being analyzed, and the electron gun is converted to pulsed operation. Also, all variable biases are removed from the ion gun.

Most Versatile Ion Source. Fig. 26 illustrates the most versatile Bendix ion source. Such a source could be used for combustion analysis, for example. When ions created outside the mass spectrometer are analyzed, a magnetic field in the ion source region is undesirable, since ions traveling with only thermal energies will be deflected away from the path through the sample inlet pinhole and the collimating slits. This trouble can be especially serious if a differentially pumped inlet system is used, since this would add more optically in-line holes and slits for the sample particles to traverse. The Bendix ion source uses a 150 gauss permanent magnet to collimate the ionizing electron beam, and this magnet can either be removed or converted to an electromagnet for the analysis of ions created outside the mass spectrometer.

Applications

Over 60 time-of-flight mass spectrometers are now being used for a variety of applications throughout the world. The type of

work being done with this instrument is illustrated by the representative applications described briefly below.

Chromatograph Effluent Identification. One of the earliest and most common uses for the time-of-flight mass spectrometer is the identification of the separated components emerging from a vapor phase chromatograph. The improvement in the separating power of a chromatograph produced by variations in the column material, column length, column temperature, and the pressure and flow rate of the carrier gas is a subject of intensive and continuing study. Unfortunately, the common method used for identifying the pure compounds emerging from the column, the measurement of retention times, is not compatible with this desirable variation in operating conditions, since the retention time itself is greatly affected by such variations. This greatly reduces the flexibility of the chromatograph, and makes desirable an independent method of identifying the emerging pure compounds.

Such an independent method of identification is provided by the mass spectrometer, which has been used with success by many workers in the field. When the Bendix Spectrometer is used in this way, it is not necessary to isolate each emerging compound in its own sample bottle for later admission to the spectrometer, except for materials with very low vapor pressures. A small fraction of the emerging gas is fed directly into the spectrometer through a needle valve. The rest of the effluent passes into the atmosphere through a hole in the valve housing. As each separated unknown emerges, its unique spectrum rises and falls on the oscilloscope screen, affording immediate identification in most cases. If it is desired to produce a permanent record of the mass spectra, photographs can be taken of the oscilloscope trace or a fast recorded spectrum (15 seconds) can be made. The relative abundance of the components can be determined by utilizing a conductivity cell in the conven-

tional manner. R. S. Gohlke of the Dow Chemical Company pioneered this application of the time-of-flight mass spectrometer, and an account of his work is in the literature.²⁸

Solids Analysis. Two experiments that illustrate solids analysis using the molecular beam inlet (Fig. 17) have been conducted at Argonne National Laboratory. One experiment²² had as its goal the derivation of the thermodynamic properties of solid and gaseous uranium monosulfide (US). This derivation was based on data supplied by several instruments, one of which was the time-of-flight mass spectrometer. A Knudsen cell sample inlet system was used with the spectrometer to vaporize US. The resulting mass spectrum showed the presence of gaseous U, S, and US (not just gaseous US), and the sizes and ratios of these mass peaks as a function of Knudsen cell temperatures up to 2200° C comprised the mass spectrometer data used for their derivation.

The other experiment²³ was designed to determine the thermodynamic properties of tungsten oxides, such as dissociation energies, heats of vaporization, and vapor pressures *vs.* temperature. A Knudsen cell sample inlet system was again used. Chemical analysis of the particular solid tungsten oxide studied mass spectrometrically gave the formula $WO_{2.96}$. The mass spectrum of gaseous tungsten oxide in equilibrium with the solid state showed the presence of WO_2 , WO_3 , W_2O_5 , $(WO_3)_2$, W_3O_8 , $(WO_3)_3$, $(WO_3)_4$, and $(WO_3)_5$. The heaviest molecule in this vapor weighed 1170 atomic mass units. The presence of molecules with an oxygen-to-tungsten ratio less than three was expected because of the composition 2.96, but the corresponding ions could have been formed by the ionizing electron beam breaking one oxygen atom away from WO_3 , $(WO_3)_2$, and $(WO_3)_3$. To determine the origin of these ions, the energy of the electron beam was continuously reduced from the usual 70 electron volts to 20 volts. The

ratio of W_3O_8 against $(WO_3)_3$ did not change during this electron energy reduction, but the ratio of W_2O_5 against $(WO_3)_3$ began to change at about 40 e.v., and at 25 e.v. no W_2O_5 ions were even detected. The WO_2 and WO_3 peaks behaved in a similar manner. These results showed that W_3O_8 was formed by thermal decomposition in the Knudsen cell, while the masses corresponding to WO_2 , WO_3 , and W_2O_5 were results of fragmentation by the electrons in the ion source.

Fast Chemical Reaction Studies. The time-of-flight mass spectrometer built by Kistiakowsky and Kydd at Harvard University (the prototype for the Bendix Model 14, Fig. 23) has been used to investigate fast chemical reactions initiated by flash photolysis³⁴ and by shock waves.³⁵

In the first experiments the open end of the fast reaction chamber (Fig. 23) was closed by a quartz window to admit the ultraviolet photolysis flash. Secondary reactions following the photolysis of CH_2CO and NO_2 were studied.

In the shock tube experiments performed by John Bradley the fast reaction chamber formed the down stream end of a small shock tube and the surface supporting the leak was the end plate of the tube from which the shock wave reflected. The mass spectrometer sampled the twice heated and compressed gas behind the reflected wave. Reactions of N_2O and CH_3NO_2 and of C_2H_2 with and without oxygen were studied in this way. The ability of the instrument to identify and measure unstable intermediates in fast reactions was illustrated by the observation of oxygen atoms from the decomposition of N_2O and of polymers of acetylene formed during its pyrolysis and oxidation.

Analysis of Water in Solids. At the Uranium Division of the Mallinckrodt Chemical Works, L. A. Fergason, D. E. Seizinger, and C. H. McBride have used their time-of-flight mass spectrometer (a Model 12-100 equipped with a recording output system) for a variety of applications.^{30, 36}

One analysis which is frequently performed at Mallinckrodt is the determination of the percentage of water present in uranium tetrafluoride. The sample is heated in a small tubular furnace through which helium is passed as a carrier gas. As the gas emerges from the furnace, a small fraction of the helium-water mixture is fed directly into the mass spectrometer through a needle valve. Over 99% of the gas stream passes into a simple rising bubble flowmeter through a hole in the valve housing. This same technique is used by many operators of the time-of-flight mass spectrometer to sample continuously the effluent from a vapor phase chromatograph. The water "memory" problem is minimized by heating the sample pipe and the ion source region of the mass spectrometer vacuum chamber to 150° C.

Calibration of the system is done by heating weighed samples of barium chloride dihydrate to 150° C in the tubular furnace. The scanner channel of the recording output system continuously monitors the m/e 18 water peak, while the controller channel continuously monitors and maintains at a constant amplitude the m/e 4 helium peak, thereby controlling the sensitivity of the instrument. The single voltage output from the scanner channel is recorded, giving a water-helium ratio. This voltage is also delivered through a voltage to analog converter to a decade scaler, which automatically integrates the water-helium ratio against time.

Amounts of water below 10 parts per million, expressed as hydrogen, in uranium tetrafluoride are routinely measured with this technique.

The temperature of the tube furnace can be programmed to increase gradually with time. A thermocouple indication of this temperature can be recorded on one channel of a two channel recorder, while the other channel records the water-helium ratio. An example suggesting the application of this arrangement uses barium chloride dihydrate

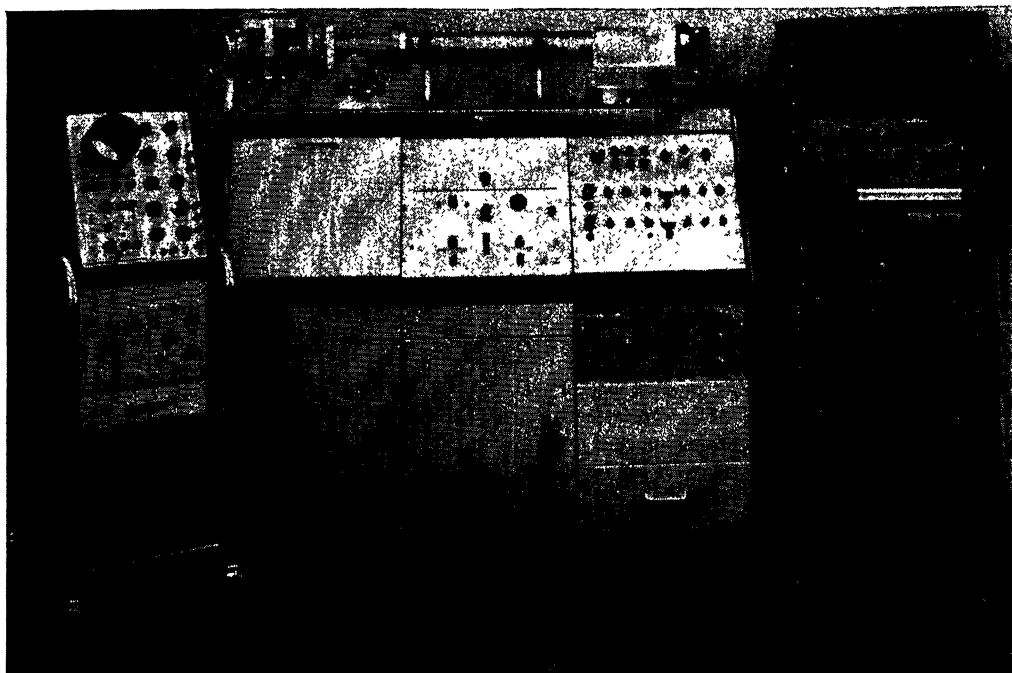


FIG. 27. Model 12-101, Bendix Mass Spectrometer, equipped with ion source S-14-107, Model 112 two channel analog output system (recording output system), and Sanborn Series 150 two channel oscillographic recorder. Tektronix Model 545 oscilloscope also shown.

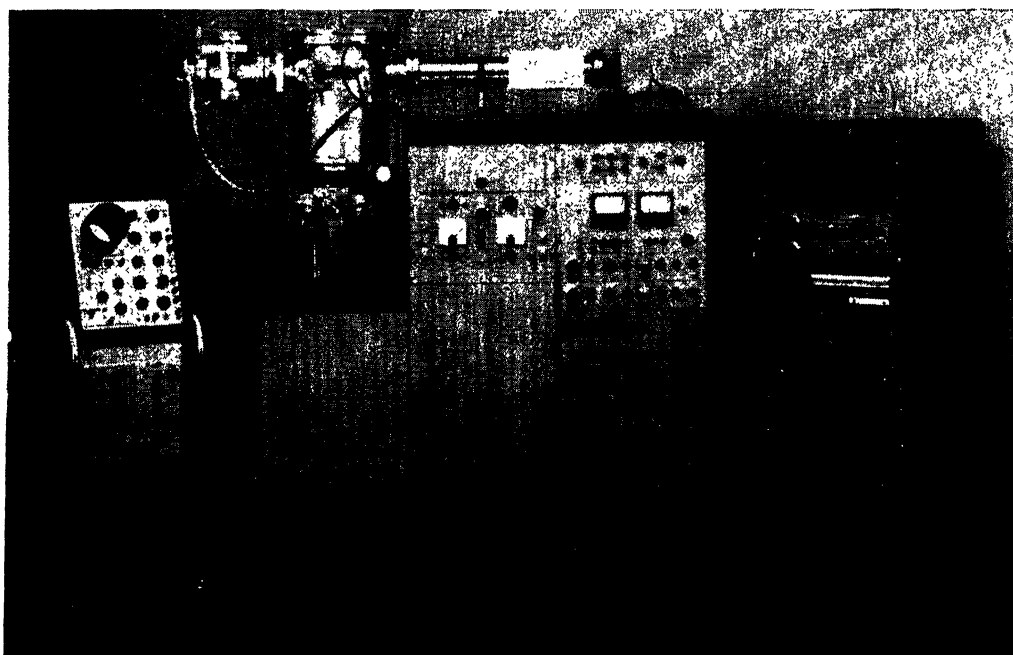


FIG. 28. Model 14-101, Bendix Mass Spectrometer, equipped as the instrument shown in Fig. 27.

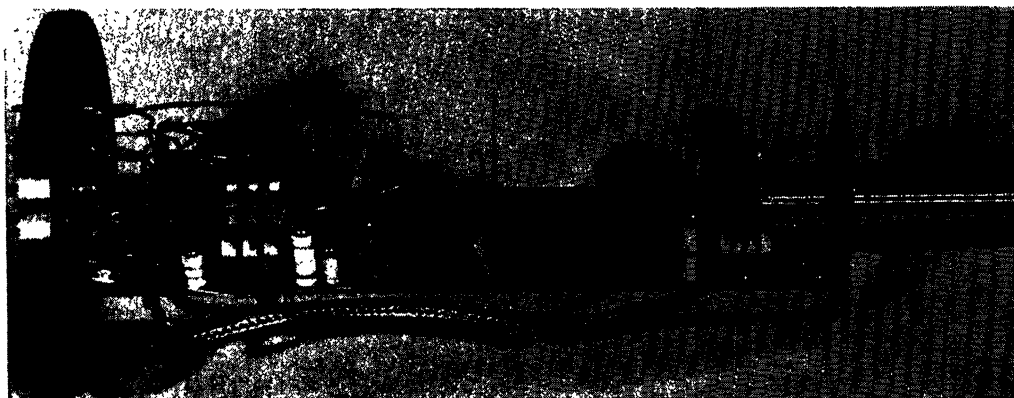


FIG. 29. Model M-105-G2 Bendix Magnetic Electron Multiplier (used with recording output system).

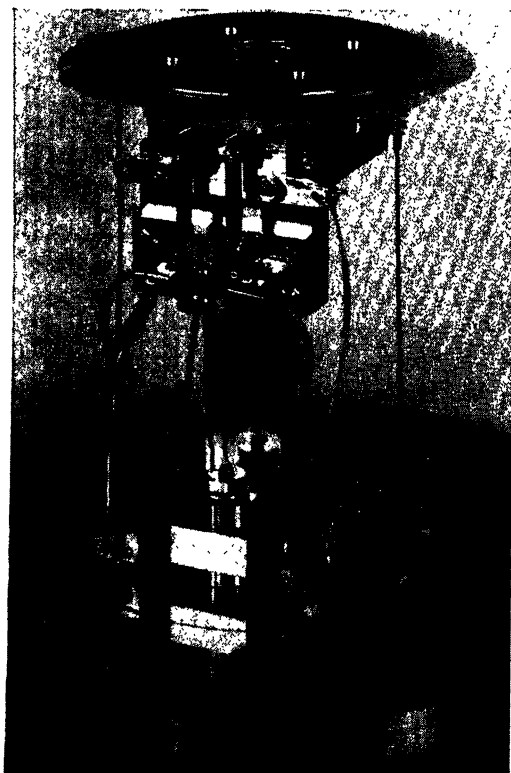


FIG. 30. Ion source S-12-100 (shown schematically in Fig. 16).



FIG. 31. Ion source S-14-101 (shown schematically in Fig. 21).

as a sample. As this powder is heated, three distinct maxima appear in the water-helium ratio. The first represents the evaporation of free water within the powder. The second

maximum represents the release of the first water molecule from the decomposing barium chloride dihydrate, while the third maximum represents the final loss of water

from this crystal. The temperatures at which these events take place is graphically shown on the two channel recording.

Figs. 27 through 31 show some standard models and components of the Time-of-Flight Mass Spectrometer manufactured by The Bendix Corporation.

REFERENCES

1. BLEAKNEY, W., AND HIPPLE, J. A., *Phys. Rev.*, **53**, 521 (1938).
2. MARINER, T., AND BLEAKNEY, W., *Phys. Rev.*, **72**, 729 (1947).
3. MARINER, T., AND BLEAKNEY, W., *Rev. Sci. Inst.*, **20**, 297 (1949).
4. ROBINSON, C. F., AND HALL, G., *Rev. Sci. Inst.*, **27**, 504 (1956).
5. ROBINSON, C. F., *Rev. Sci. Inst.*, **27**, 509 (1956).
6. BENNETT, W. H., *J. App. Phys.*, **21**, 143 (1950).
7. TOWNSEND, J. W., *Rev. Sci. Inst.*, **23**, 538 (1952).
8. DEKLEVA, J. AND PETERLIN, A., *Rev. Sci. Inst.*, **26**, 399 (1955).
9. PETERLIN, A., *Rev. Sci. Inst.*, **26**, 398 (1955).
10. WHERRY, T. C., AND KARASEK, F. W., *J. App. Phys.*, **26**, 682 (1955).
11. HOLMES, J. C., *Rev. Sci. Inst.*, **28**, 290 (1957).
12. DEKLEVA, J., AND RIBARIC, M., *Rev. Sci. Inst.*, **28**, 365 (1957).
13. DONNER, W., *App. Spec.*, **8**, 157 (1954).
14. DONNER, W., *ISA Journal*, **3**, 89 (1956).
15. HIPPLE, SOMMER, AND THOMAS, *Phys. Rev.*, **76**, 1877 (1949).
16. SOMMER, THOMAS, AND HIPPLE, *Phys. Rev.*, **82**, 697 (1951).
17. BERRY, C. E., *J. App. Phys.*, **25**, 28 (1954).
18. ALPERT, D., AND BURITZ, R. S., *J. App. Phys.*, **25**, 202 (1954).
19. EDWARDS, A. G., *Brit. J. Applied Phys.*, **6**, 44 (1955).
20. BRUBAKER, W. M., AND PERKINS, G. D., *Rev. Sci. Inst.*, **27**, 720 (1956).
21. HAYS, E. E., RICHARDS, P. I., AND GOUDSMIT, S. A., *Phys. Rev.*, **84**, 824 (1951).
22. SMITH, L. G., *Rev. Sci. Inst.*, **22**, 166 (1951).
23. CAMERON, A. E., AND EGGERS, D. F., JR., *Rev. Sci. Inst.*, **19**, 605 (1948).
24. WOLFF, M. M., AND STEPHENS, W. E., *Rev. Sci. Inst.*, **24**, 616 (1953).
25. KATZENSTEIN, H. S., AND FRIEDLAND, S. S., *Rev. Sci. Inst.*, **26**, 324 (1955).
26. WILEY, W. C., AND MCLAREN, I. H., *Rev. Sci. Inst.*, **26**, 1150 (1955).
27. WILEY, W. C., *Science*, **124**, 817 (1956).
28. GOHLKE, R. S., *Anal. Chem.*, **31**, 535 (1959).
29. *Chemical Week*, Dec. 21, 1957, p. 61.
30. FERGASON, L. A., SEIZINGER, D. E., AND MCBRIDE, C. H., Mallinckrodt Chemical Works 1433, Process Development Quarterly Report, November 2, 1959, unclassified.
31. FOOTE, T., AND HARRINGTON, D. B., *Rev. Sci. Inst.*, **28**, 585 (1957).
32. CATER, E. D., GILLES, P. W., RAUH, E. G., AND THORN, R. J., to be published.
33. ACKERMANN, R. J., RAUH, E. G., AND THORN, R. J., to be published.
34. KISTIAKOWSKY, G. B., AND KYDD, P. H., *J. Am. Chem. Soc.*, **79**, 4825 (1957).
35. BRADLEY, J. N. AND KISTIAKOWSKY, G. B., *J. Chem. Phys.*, to be published.
36. MCBRIDE, C. H., FERGASON, L. A., AND SEIZINGER, D. E., Mallinckrodt Chemical Works, private communication.

D. B. HARRINGTON

MICROWAVE SPECTROSCOPY

ATOMIC FREQUENCY STANDARDS

General Considerations

A discussion of frequency immediately involves a discussion of time because of the reciprocal relationship between the two quantities. Astronomical events such as the mean solar day and, since 1956, the tropical

year have been used for reasons of permanence and continuity as standards for the time scale, that is the origin and the size of the unit. The need, however, to interpolate these rather large units has led to quartz oscillators of great stability and to techniques of intercomparing frequencies to greater precision than any other physical

quantity, and such oscillators can thus be used to provide very uniform time scales if properly calibrated against the standard. In calibrating these oscillators against the mean solar day, for example, variations were detectable in the latter. In using astronomical standards, furthermore, a very long time is required to attain high precision for the fundamental reason that in counting cycles many counts are required to reduce the random errors in marking the beginning and end of a cycle.

As a possible alternative, the observed transition frequencies of atomic systems, given by the Bohr relation,

$$h\nu = \Delta E, \quad (1)$$

appeared capable of satisfying the general requirements of a standard so well that it became conceivable to take the corresponding period as the standard of the unit of time, or even to make frequency a basic quantity and consider time a derived quantity. In the standard for any unit we require constancy of the determination of the size of the unit with time. In an astronomical standard the size of the cycle may vary; or if this objection is overcome by specifying one particular cycle, such as the tropical year for 1900, the determination of this unit from subsequent observations may fail from inadequate knowledge of the motion. The requirement of constancy is more likely to be met in a small system of elementary particles such as an atom than in a macroscopic system such as the sun-earth-moon system

because of the smaller number of particles involved and because of the possibility of arranging that the perturbing energies be much smaller than the system energy.

A good standard must also be observable with precision. If we suppose that the process of measuring a frequency is equivalent to taking the mean of the distribution of frequencies comprising a spectral line such as shown in Fig. 1, we have

$$\bar{\omega} = \int \omega g(\omega) d\omega. \quad (2)$$

The line, $g(\omega)$, may be expressed as

$$g(\omega) = y_0(\omega - \omega_0) + \eta y(\omega - \omega_0), \quad (3)$$

where $\eta y(x)$ is one of the ensemble of functions describing departures from the ideal shape, $y_0(x)$, because of noise or other disturbance, and η is a parameter of smallness. The resonant frequency of any one determination is ω_0 , also considered one of an ensemble to account for experimental variations. Clearly $\bar{\omega}$ will have a distribution, $f(\bar{\omega})$, due to variations in ω_0 (drifts) and in the form of y (disturbances). For a good standard we seek to achieve the smallest value of

$$\sigma^2 = \overline{(\bar{\omega} - \bar{\omega})^2} = \bar{\omega}^2 - \bar{\omega}^2, \quad (4)$$

where

$$\bar{\omega} = \int \bar{\omega} f(\bar{\omega}) d\bar{\omega} \quad \text{and} \quad \bar{\omega}^2 = \int \bar{\omega}^2 f(\bar{\omega}) d\bar{\omega}. \quad (5)$$

This problem may be attacked in special cases by usual statistical methods; but we can say immediately that narrow $y_0(\omega - \omega_0)$, small η or good signal-to-noise ratio, and stable ω_0 or freedom from drift and perturbations will help. Atomic frequency standards offer all these possibilities.

Astronomical standards offer the advantages of permanent availability and continuity. Atomic standards offer an equivalent advantage of renewability in case of loss, but in case of a lapse of continuity the origin may be lost. This is a disadvantage, how-

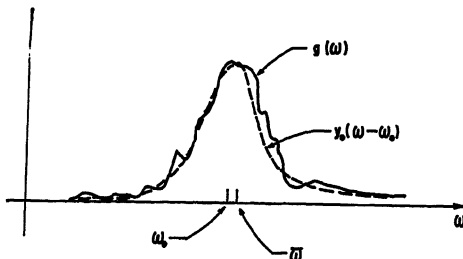


FIG. 1. Hypothetical spectral line showing possible variations in observation.

ever, only in experiments extending over decades, as conducted in positional astronomy.

A good standard must be of optimum size for comparison, as are the meter and the kilogram. Since time standards always are nearly of the form $f(t) = f(t + 2\pi n/\omega)$ and we have to average over large values of n for precision or to take the Fourier frequency transform of a large number of cycles, ω should be large so that these operations can be applied to conveniently small intervals. Furthermore, because of the characteristics of practical electrical circuits, frequencies of many cycles per second are much more convenient to multiply and divide electronically than are frequencies of one cycle per day or per year. Since frequency measurement is essentially a counting process, we also note that the standard must not be too rapid for counting in some fashion. This effectively limits us to frequencies below about 300 kMc at the present state of the art.

To summarize, we seek a narrow, intense transition in the range of microwave or radio frequency spectroscopy, insensitive to perturbing fields, and observable with apparatus that remains stable for times necessary to secure a sufficiently narrow band width of observation, typically of the order of some tens of seconds.

Two transitions exist with outstanding characteristics. These are the ($J = 3, K = 3$) inversion of $N^{14}H_3$ at 23,870 Mc useful for its high intensity and convenient frequency, and the ($F = 4, m_F = 0$) $\leftrightarrow$ ($F = 3, m_F = 0$) transition between hyperfine levels in the ground state of Cs^{133} at 9,192 Mc arising from electron spin-nuclear spin interaction, useful for its insensitivity to electric and magnetic fields and also its convenient frequency. Other transitions which have been studied are the ($J = N \pm 1$) $\rightarrow$ ($J = N$) transitions near 60,000 Mc in the ground state of oxygen arising from change of electronic spin momentum with respect to rotational momentum, and the hyperfine transi-

tions in the ground state of the alkali metals Na^{23} at 1,772 Mc and Rb^{87} at 6,835 Mc.

Techniques of Observation

Gas Absorption.¹ The gas absorption cell was historically the first method of utilizing molecular resonances for a frequency standard and was used for NH_3 and O_2 . For a well isolated pressure broadened line a sufficiently good expression is given by the Van Vleck-Weisskopf formula for the absorption per unit length, γ :

$$\gamma = \frac{8\pi^2 N f}{3ckT} |\mu_{ij}|^2 \left[\frac{1/2\pi\tau}{(\nu - \nu_0)^2 + (1/2\pi\tau)^2} + \frac{1/2\pi\tau}{(\nu + \nu_0)^2 + (1/2\pi\tau)^2} \right], \quad (6)$$

where N is the number of molecules per unit volume; f is the fraction of molecules in the lower state i , of energy W_i , usually given as

$$e^{-W_i/kT} / \sum_i e^{-W_i/kT};$$

$|\mu_{ij}|^2$ is the mean square matrix element for transitions from i to j ; c , k , T , and ν have their usual significance; and τ is the mean time between collisions, varying inversely as pressure. The half width of the line at the half intensity point, $\Delta\nu$, is $1/2\pi\tau$. Standard techniques of microwave spectroscopy are used, namely, a microwave generator, absorption cell containing gas under low pressure for well resolved lines, and a microwave power detector arranged to display absorption *vs.* frequency. Many refinements have been devised to improve the precision of measurement such as modulation of the source and the absorption and various bridge arrangements to improve minimum detectable frequency change.

A practical NH_3 device gave frequency precision of about 2 parts in 10^8 over 8 days, and an O_2 spectrometer gave actual frequency measurements to 2 parts in 10^8 and evidence of greater precision at the cost of engineering refinements to reduce residual systematic errors.

The limitations of the gas absorption standard are large $\Delta\nu$ of some tens of kilocycles due to pressure and Doppler broadening and consequent inability to localize the line precisely because of systematic errors which usually limit measurement to a fixed fraction of a line width. Consequently the gas absorption standard has essentially been abandoned as an atomic frequency standard.

Atomic Beam.² The atomic beam frequency standard has proved the most satisfactory instrument to date probably because it most closely approaches the ideal of a single atom in field-free space, unperturbed by collisions and free of Doppler effect. Fixed laboratory installations serving as national standards and also portable commercial models have been made. The usual arrangement is shown in Fig. 2. Atoms in all sub-levels of both states $F = 3$ and $F = 4$ leave the oven with a distribution of velocity vectors and are deflected in the moderately strong non-uniform Stern-Gerlach field by

virtue of an effective component of dipole moment along the field, dependent on both m_F and field. For the two $m_F = 0$ levels the deflection is equal and opposite. The atoms then drift in the low-field space C and are subject to a Ramsey-type excitation using separated r-f fields. At resonance change of state occurs by absorption or stimulated emission depending on the initial state, and upon traversing the second identical deflecting field only those atoms having undergone transitions are focused on the detector. If resonant transitions do not occur, the beam is deflected away from the detector. Atoms with $m_F \neq 0$ undergo no transitions and never reach the detector. Detection is commonly accomplished by ionization of the alkali atoms striking a hot wire and observation of the resulting current by as convenient and sensitive means as possible. The line width is governed by the uncertainty principle, $\Delta E \Delta t \geq \hbar/2$ or $\Delta\nu \Delta t \geq 1/4\pi$, where Δt is the time of flight of the atom.

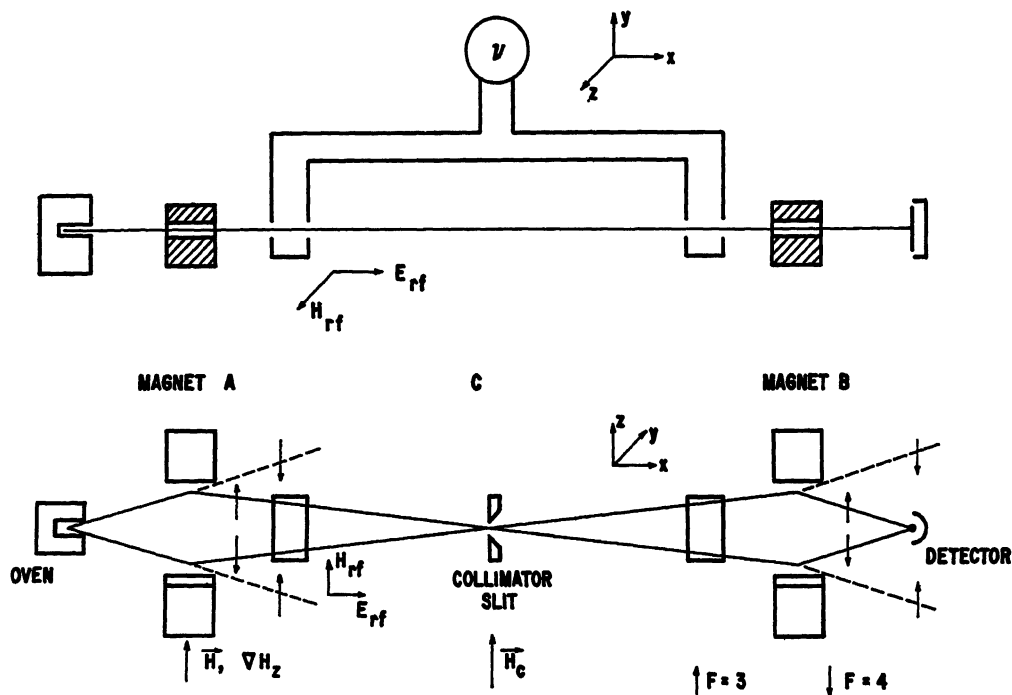


FIG. 2(a)

The Cs beam has been found to be self-checking as to correct phase of the two r-f exciting fields and satisfactorily insensitive to experimental conditions such as value of oven temperature, beam flux, chamber pressure, Stern-Gerlach field, Stark fields, r-f power level, mechanical alignment, and C field. Only the latter parameter is corrected for by the relation,

$$\nu = (\nu_0 + 427 \text{ H}^2) \text{ sec}^{-1}, \quad (7)$$

representing an accurate correction of a few parts in 10^{10} . Precision may be increased by lengthening the beam until various non-fundamental systematic effects such as attainable vacuum, focusing, and spectral impurity, that is, phase jitter of the exciting radiation, become important. First-order

Doppler shift or broadening is absent since the particle direction and photon direction are perpendicular.

Results with several beams of independent design of 50 cm length have shown that the resonance can be reproducibly observed on a given apparatus to about 1 part in 10^{10} , and that these apparatuses agree among themselves to 3 or 4 parts in 10^{10} . With additional care in construction and testing it has recently been possible to obtain precision of measurement of 2 parts in 10^{12} as estimated by the standard deviation of the mean, to obtain agreement between two apparatuses to 2 parts in 10^{11} , and to assign the uncertainty of approaching the idealized Cs resonance to 2 parts in 10^{11} .

As to current developments, somewhat



(b)

FIG. 2. Cesium beam atomic frequency standard. (a) Schematic. (b) Apparatus at Boulder Laboratories, National Bureau of Standards, by permission of R. C. Mockler.

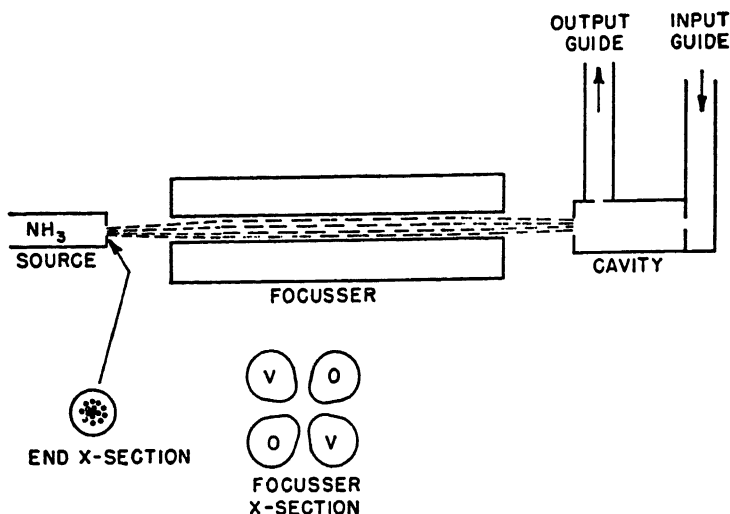


FIG. 3. Ammonia maser [After Gordon, Zieger, and Townes, *Physical Review*, **95**, 282 (1954)].

longer beams of 1.5 to 5 m length have been made recently; and the resonance of Ti^{205} at 21, 311 Mc has been suggested as worth investigating.

Maser.³ The gas maser may also be considered an atomic frequency standard. Figure 3 shows one experimental arrangement. Ammonia atoms leave the oven in a beam and are prepared in the upper inversion state by the quadrupolar electrostatic focuser which focuses atoms in the upper state and defocuses those in the lower state; the focused atoms enter the microwave cavity where they are stimulated to emit by the existing microwave field. This energy is stored in the cavity to produce further stimulated emission and to supply losses of the cavity and external loads. The maser can selectively amplify an applied signal in the neighborhood of resonance or it can oscillate. In the former case the line width depends on experimental conditions of beam flux, cavity Q , and applied signal strength and may be of the order of a few kilocycles. In the latter case the condition for oscillation is that the energy input per unit time equal or exceed the power losses P , or

$$nP_{2 \rightarrow 1}h\nu \geq P, \quad (8)$$

where n is the number of excited molecules entering the cavity per unit time and $P_{2 \rightarrow 1}$ is the probability that a molecule undergo stimulated emission while in the cavity. Expressing $P_{2 \rightarrow 1}$ in terms of the dipole matrix element μ connecting states 1 and 2, the energy density, the time spent in the cavity $\tau = l/v$, and the line width $\Delta\nu \sim 1/\tau$, and expressing P in terms of the loaded Q and the stored energy in the volume V , we find the minimum beam flux for oscillation to be

$$n_{\min} \sim Vh/\mu^2Q\tau^2. \quad (9)$$

$P_{2 \rightarrow 1}$ may be made of the order of $1/2$ for strong oscillations, and some 10^{-9} w may be extracted. The spectral output of the maser oscillator is exceedingly monochromatic; its relative half-half width is given by

$$\frac{\delta\nu}{\nu} = \frac{4\pi kT(\Delta\nu)^2}{P\nu} \quad (10)$$

and observed in practice as a few parts in 10^{12} —better than any other r-f source. The actual frequency is sensitive to experimental conditions of cavity tuning, cavity Q , beam flux, and Doppler shift due to possible existence of traveling waves in the cavity which supply localized losses such as an exit iris. These conditions must be specified more

carefully than the Cs conditions in order to achieve comparable reproducibility to parts in 10^{10} .

An interesting application may be to solve the limitation of spectral purity in the Cs exciting radiation by deriving it from a maser oscillator.

Optical Pumping.⁴ As in the atomic beam and the maser, atoms are prepared in a pure state arranged to have a long lifetime and are stimulated to emit by microwave radiation in a manner free of Doppler effect; and the change of state is detected. Here the state preparation consists of selective excitation of a vapor at partial pressure of about 10^{-7} mm Hg from some of its ground state magnetic or hyperfine sublevels to an upper electronic state by specially filtered or polarized optical resonance radiation. Excited atoms become more or less equally distributed among the sub-levels of the upper state by collisions and spontaneously radiate to all lower levels. In the case of the alkali atoms it is possible to enhance the upper hyperfine level of the ground state at the expense of the lower.

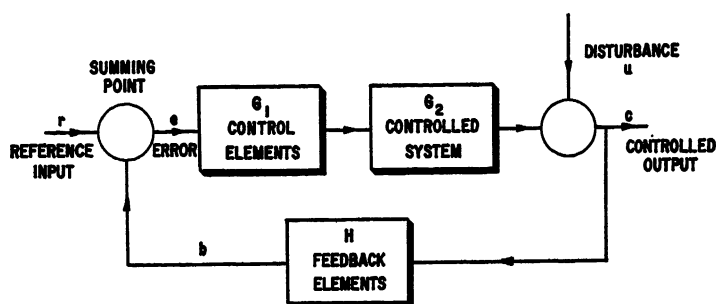
This situation is preserved because collisions in the ^3S ground state with either a buffer gas introduced at about 100 mm Hg or a special wall coating are not disorienting because of absence of magnetic dipole or spin exchange interactions, and the requisite long lifetime of the prepared state is accomplished. Doppler width reduction occurs essentially by a mechanism⁵ in which the radiating atom is confined by buffer gas collisions to a region small compared to a wavelength, so that the motion of the source does not cumulatively affect the phase of the emitted wave, as is ordinarily responsible for Doppler effect. If $\Delta F = 1$ transitions are induced between these hyperfine levels by microwave radiation, the fact can be detected by a change in the absorption, scattering, or polarization of the exciting optical radiation because of the altered populations produced.

Microwave responses as narrow as 400

cps for Na, 40 cps for Cs, and 20 cps for Rb have been observed. Present limitations are a non-negligible shift in line frequency with buffer gas composition, pressure, and temperature, so that the device does not seem to provide as ideal a standard as an atom in a beam, but nevertheless does provide a very stable frequency with relatively small apparatus.

Utilization of Resonance

The utilization of an atomic resonance as a frequency standard may consist of passive use, as a cavity resonator might be used as a wavemeter, or of use of the frequency discrimination available in the line as a part of a control mechanism to regulate an oscillator continuously. Such control mechanisms may possess considerable electronic complexity and sophistication, but they may usually be brought into the standard form shown in Fig. 4 with either phase or frequency as the controlled variable. Figure 5 shows a loop which may be used to phase lock an oscillator to a maser. The reference quantity is the phase of the maser output, $\omega_L t$. To simplify analysis it is convenient to assume that the reference frequency is re-supplied through the disturbance input, so that inside the loop we deal only with quantities proportional to phase error. The relative stability of the auxiliary conversion oscillator introduced into the sum point, $\delta\omega_L/\omega_L$, enters into the system relative stability, $\delta\omega/\omega$; but it is reduced by the factor ω_L/ω , which may be chosen as small as 10^{-3} or 10^{-4} . From the condition on the figure, $(\omega - \omega_r - \omega_L)t < \pi$, and the assumption $\delta\omega_r = 0$, we have at sufficiently long times $\delta\omega = \delta\omega_L$ or $\delta\omega/\omega = (\delta\omega_L/\omega_L)(\omega_L/\omega)$. The same loop might be used to control an oscillator from the Cs resonance. The reference frequency would be provided passively by the property of Cs; the sum point would be a convenient schematic fiction containing no apparatus; and the phase transducer would be replaced by one of a variety of frequency



$$e = b - r$$

$$c = G_1 G_2 (Hc - r) + u$$

FIG. 4. Standard form of control mechanism.

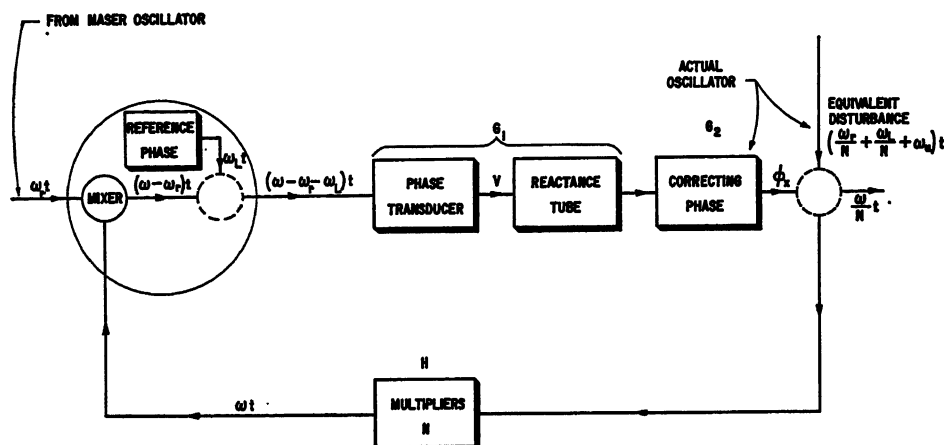


FIG. 5. Oscillator phase locked to a maser, drawn as a control mechanism. Phase is the controlled quantity.

discriminators, transducing frequency difference into a control voltage.

Applications

Atomic frequency standards have provided orders of magnitude improvement in the scientific time scale. When compared with the most refined mean solar second, the Cs beam confirmed variations in the latter of the order of 5 parts in 10^9 in the course of a year, and contributed to a redefinition of the second in 1956 by the Comité International des Poids et Mesures (CIPM) as the fraction $1/31,556,925.9747$ of the trop-

ical year for January 0, 1900, at 12 hours Ephemeris Time. This unit, although constant by definition, is very cumbersome to recover from current astronomical observations; therefore as a result of a recent measurement⁶ yielding

$$\nu_{Cs} = (9,192,631,770 \pm 20) \text{ sec}^{-1} \text{ (of E.T.)}$$

the second may be considered to be provided immediately by the Cs resonance to the stated accuracy. Because different Cs resonators are now constant among themselves to a precision of a few parts in 10^{10} , with early expectation of order of magnitude improve-

ment, the CIPM may eventually define a unit of time based on an atomic frequency standard, similar to its intended action with respect to an atomic unit of length in 1960.

Several applications to physical experiments exist. First, a signal of great spectral purity such as that available from a maser may be used as a high resolution analyzer of other spectra such as those produced by electronic oscillators and multipliers.⁷ For if $f_1(t)$ is the signal from the oscillator and $f_2(t)$ is the signal from the maser, we may form $f_1(t)f_2(t)$ whose Fourier transform is the convolution integral

$$\frac{1}{2\pi} \int F_1(s)F_2(\omega - s) ds,$$

where $F(s)$ is the Fourier transform of $f(t)$; and if F_2 may be approximated by the Dirac delta function, we may arrive at $|F_1(\omega)|^2$, the power spectrum of f_1 .

The great precision in frequency measurement does not, of course, contribute to measurement of physical quantities involving dimensions other than time; for these are limited by the lesser precision available in length, mass, or current, as the case may be. The precision may, however, be utilized by selecting quantities involving frequency or time alone, such as the cyclotron frequency of the electron or proton, or the frequency of nuclear precession in a magnetic field, or dimensionless ratios of such frequencies. One such experiment⁸ has tested anew the postulate of special relativity prohibiting a preferred frame among frames in uniform relative motion by observing the rate of a beam maser for molecular velocity along and against the orbital velocity of the earth. The experiment is equivalent to the Michelson-Morley experiment, which gave a null result of 1/20 of the expected ether drift. The present experiment improved this to 1/1000 by virtue of the ability to compare frequencies precisely.

In addition, the precision inherent in frequency determination may be used to ob-

tain a number of quantities external to the atom upon which ΔE in Equation (1) depends, such as Stark or Zeeman fields, initial momentum $m\mathbf{u}$ of the system (Doppler effect), and the gravitational scalar and vector potential, χ and γ , at the emitter, depending on the metric tensor g_{ik} . Calculations may most conveniently be carried out separately according to the predominant effect. Møller⁹ gives for the observed frequency of emission in the absence of electric and magnetic fields:

$$\begin{aligned} h\nu &= \frac{[\dot{m}_0^2 - \ddot{m}_0^2]c^2c'^2}{2E(1 - c'\mathbf{u} \cdot \mathbf{e}/E)} \\ &= (\dot{m}_0 - \ddot{m}_0)c^2 \frac{1 - (m - \dot{m}_0)/m}{(1 - \gamma \cdot \mathbf{u}/c')(1 - mc'\mathbf{u} \cdot \mathbf{e}/E)} \end{aligned} \quad (11)$$

where $\dot{m}_0$ and $\ddot{m}_0$ are rest masses in an inertial frame for initial and final states; $c' = c(1 + 2\chi/c^2)^{1/2}$; c is the velocity of light in an inertial frame; $E = mc'^2(1 - \gamma \cdot \mathbf{u}/c')$ is the energy of the initial state;

$$m = \dot{m}_0/[(\sqrt{1 + 2\chi/c^2} - \gamma \cdot \mathbf{u}/c)^2 - u^2/c^2]^{1/2};$$

and $\mathbf{e}$ is the unit vector in the direction of photon emission. For systems at rest at places differing by gravitational potential $\Delta\chi$, Equation (11) predicts a relative frequency shift of $\Delta\chi/c^2$, the Einstein gravitational red shift. This effect is 1.76 parts in 10^{13} per mile at the surface of the earth. If one of the systems is put into an artificial satellite, the result is complicated by the relativistic Doppler effect arising from the velocity dependence in Equation (11) and the need to integrate both effects over the orbit; but the effect has been calculated as a few parts in 10^{10} for a typical satellite. Both magnitudes are within reach by present atomic frequency standards. Such implications of general relativity as to the alteration of time scales may have practical application to accurate timekeeping among space stations.

REFERENCES

1. LYONS, H., "Spectral Lines as Frequency Standards," *Ann. N. Y. Acad. Sci.*, **55**, 831 (1952).

- K. SHIMODA, "Atomic Clocks and Frequency Standards on an Ammonia Line. I, II, and III," *J. Phys. Soc. Japan*, **9**, 378, 558, 567 (1954). C. H. TOWNES AND A. L. SCHAWLOW, "Microwave Spectroscopy," McGraw-Hill, New York (1955). JOHN M. RICHARDSON, "Experimental Evaluation of the Oxygen Microwave Absorption as a Possible Atomic Frequency Standard," *J. Appl. Phys.*, **29**, 137 (1958).
2. RAMSEY, NORMAN F., "Molecular Beams," Clarendon Press, Oxford (1956). L. ESSEN AND J. V. L. PARRY, "The Cesium Resonator as a Standard of Frequency and Time," *Phil. Trans. Roy. Soc. London*, **A250**, 45 (1957). J. HOLLOWAY, W. MAINBERGER, F. H. REDER, G. M. R. WINKLER, L. ESSEN, AND J. V. L. PARRY, "Comparison and Evaluation of Cesium Atomic Beam Frequency Standards," *Proc. Inst. Radio Engrs.*, **47**, 1730 (1959). R. C. MOCKLER, R. E. BEEHLER, AND J. A. BARNES, "An Evaluation of a Cesium Beam Frequency Standard," in "Quantum Electronics—A Symposium," C. H. TOWNES, ed., Columbia Univ. Press, New York (1960). R. C. MOCKLER, R. E. BEEHLER, AND C. S. SNIDER, "Atomic Beam Frequency Standards," *Inst. Radio Engrs. Trans. on Instrumentation* (to be published).
3. GORDON, J. P., ZEIGER, H. J., AND TOWNES, C. H., "The Maser—New Type of Microwave Amplifier, Frequency Standard, and Spectrometer," *Phys. Rev.*, **99**, 1264 (1955). N. G. BASOV AND A. M. PROKHOROV, "The Theory of the Molecular Generator and Power Amplifier," *Proc. Acad. Sci. (U. S. S. R.)*, **101**, 47 (1955). K. SHIMODA, T. C. WANG, AND C. H. TOWNES, "Further Aspects of the Theory of the Maser," *Phys. Rev.*, **102**, 1308 (1956). J. BONANOMI, J. DE PRINS, J. HERRMANN, AND P. KARTASCHOFF, "Stabilite d'Etalons de Fréquence à NH_3 ," *Helv. Phys. Acta*, **30**, 288 (1957). R. C. MOCKLER, J. BARNES, R. BEEHLER, H. SALAZAR, AND L. FEY, "The Ammonia Maser as an Atomic Frequency and Time Standard," *Trans. Inst. Radio Engrs.*, **1-7**, 201 (1958). J. WEBER, "Masers," *Rev. Modern Phys.*, **31**, 681 (1959).
4. KASTLER, A., "Optical Methods of Atomic Orientation and of Magnetic Resonance," *J. Opt. Soc. Am.*, **47**, 460 (1957). M. ARDITI AND T. R. CARVER, "Optical Detection of Zero-Field Hyperfine Splitting of Na^{23} ," *Phys. Rev.*, **109**, 1012 (1958). E. C. BEATTY, P. L. BENDER, AND A. R. CHI, "Narrow Hyperfine Absorption Lines of Cs^{133} in Various Buffer Gases," *Phys. Rev.*, **112**, 450 (1958). P. L. BENDER, E. C. BEATTY, AND A. R. CHI, "Optical Detection of Narrow Rb^{87} Hyperfine Absorption Lines," *Phys. Rev. Letters*, **1**, 311 (1958).
5. WITTEKE, J. P. AND DICKE, R. H., "Redetermination of the Hyperfine Splitting in the Ground State of Atomic Hydrogen," *Phys. Rev.*, **103**, 620 (1956).
6. MARKOWITZ, W., HALL, R. G., ESSEN, L., AND PARRY, J. V. L., "Frequency of Cesium in Terms of Ephemeris Time," *Phys. Rev. Letters*, **1**, 105 (1958).
7. MOCKLER, BEEHLER, AND BARNES, "An Evaluation of a Cesium Beam Frequency Standard," loc. cit.
8. CEDARHOLM, J. P., BLAND, G. F., HAVENS, B. L., AND TOWNES, C. H., "New Experimental Test of Special Relativity," *Phys. Rev. Letters*, **1**, 342 (1958).
9. MØLLER, C., "On the Possibility of Terrestrial Tests of the General Theory of Relativity," *Nuovo cimento*, Series X, **6 Supp.**, 381 (1957).

JOHN M. RICHARDSON

THEORY, INSTRUMENTATION, APPLICATIONS

The portion of the electromagnetic spectrum extending approximately from one millimeter (300,000 megacycles) to 30 centimeters (1,000 megacycles) is designated the microwave region. This region lies between the far infrared and the conventional radio-frequency regions. Spectroscopic applications of microwaves consist almost exclusively of absorption work in gaseous samples, not of emission work since emission spectra have been observed only from astronomical sources.

With some exceptions the various types of spectra are distinguished by the energy origins. In the visible and ultraviolet regions the transitions between electronic energy states are directly measurable as characteristic of elements with vibrational and rotational energies of molecules observed only as perturbation effects. In the infrared region the vibrational spectra are observed directly as characteristic of functional groups with rotational energies observed as perturbation effects. In the microwave region transitions

between rotational energies of molecules are observed directly as characteristic of absorbing molecules as a whole with nuclear effects as first-order perturbations; whereas in the radio-frequency (rf) region, the nuclear effects are directly observable. Microwave spectroscopy, a science only about 15 years old, has created new interest in Stark and Zeeman effects (electric and magnetic field effects upon spectra) and in hyperfine structure of molecular spectra. Intermolecular interactions are observed from measurements of widths and shapes of spectral lines. Especially important today is the observation in the microwave region of *paramagnetic resonance absorption* (PMR). Here the paramagnetic substance is placed in a magnetic field, and the precession of the electric momentum vector about the field then occurs. The interaction energy of the magnetic moment of the ion or molecule with the external field is quantized; transitions between the different Zeeman levels (different orientation of the electronic momentum vector in the external electric field) give rise to absorption in the microwave region with the magnetic fields of the order of a few kilogauss at the proper value. Thus there is close analogy to *nuclear magnetic resonance* (NMR) observed in the rf region; PMR provides important information in crystal structures, chemical bonding, electronic state of ions in crystals and nuclear hyperfine structure.

Liquids and solutions have broad absorption peaks in the microwave region associated with anomalous dispersion caused by orientation of molecular dipoles in the field of radiation. These peaks occur at frequencies of $\frac{1}{2}\pi\tau$, where τ is the relaxation time of the dipole. Thus, with the theory of Debye calculations can be made of relaxation time, dipole moment and dielectric constant of complex compounds. Structural information concerning bond lengths, bond angles and nuclear masses may be calculated. Nuclear spin and quadrupole coupling information is

obtained from data on the fine structure of some absorption bands. Internal rotation, hindered and unhindered, of organic molecules is evaluated. The sharp absorption spectrum lines may be used to control the frequency of an oscillator; as secondary frequency standards; and for stabilization of magnetic fields. An atomic clock, in which the frequency of a particular line of ammonia gas serves as the standard, provides true accuracy of one part in ten million, somewhat better than time standards based on rotation of the earth.

So the largest and most important use is coming to be the qualitative and quantitative analysis of complex chemical compounds, including isotope analysis. Thus the spectrum of Cl^{35}CN is as easily distinguished from Cl^{37}CN as it is from CH_3OH , because the frequencies of the rotational spectra in the microwave region are inversely proportional to the moments of inertia of the molecules, and hence these frequencies vary directly with changes in isotopic mass. For chemical analysis a listing of 3 frequencies usually identifies a particular chemical uniquely; the spectral space available for chemical identification in the range of 20,000 to 220,000 Mc, allowing $\frac{1}{3}$ Mc for resolution of each line is 600,000. The usual spectrometer sensitivity allows detections of gases at a dilution of 100 to 1, but N^{14}H_3 may be found in a dilution of 1 in 10 million. Because the spectrometers operate at a very low pressure, less than 1 micromole of a sample is required for qualitative analysis.

As in any other type of absorption spectroscopy, the apparatus required in microwave spectroscopy consists essentially of a source of radiation, a sample cell and a detector. Unlike the optical spectrometer which depends on the element of dispersion—a prism or grating, the microwave spectrometer, a completely electronic instrument, requires no dispersive component because the source is monochromatic, the frequency of which can be varied at will and measured

MONOCHROMATORS

electronically with very high precision. The most common type of microwave source is the klystron, a specially designed high vacuum electron tube. The klystron output is monochromatic under any given set of conditions, so no separate monochromator is required in microwave spectroscopy. The frequency of the output of any klystron may be varied somewhat by mechanical and/or electrical adjustment, and different types are available to cover various portions of the microwave spectrum. The sample cell usually consists of a wave guide, a long metal tube with rectangular cross section. Typical dimensions are 20 feet long and one inch by one-half inch in cross section. The detector usually consists of a silicon crystal, although bolometers and other heat-type detectors are occasionally used.

In addition to these three basic components, a complete typical microwave spectrometer includes provision for modulation of the absorption spectrum, an a-c amplifier for the detector output, a final indicator consisting either of a cathode ray oscilloscope or a strip recorder, a sweep generator

to vary synchronously the source frequency and one axis of the final indicator, a means of frequency measurement, a gas sample handling system, and the necessary electronic power supplies. The modulation is necessary in order to obtain sufficient sensitivity in the measurements, and is commonly based upon the Stark effect. The a-c amplifier must be tuned to the frequency of modulation. Methods of measuring frequencies in the microwave region can be accurate to within one part in several million. A detailed account of apparatus components is to be found in reference 1; many improvements and modifications have been reported in subsequent papers in *Physical Review* and other periodicals. [Abridgement of an article by Dr. Robert B. Fisher in the "Encyclopedia of Chemistry."]

REFERENCE

1. GORDY, WALTER, SMITH, WM. V., AND TRABULO, RALPH F., "Microwave Spectroscopy," John Wiley and Sons, Inc., N. Y., pp. 446, 1953.

GEORGE L. CLARK

MONOCHROMATORS

As the name indicates, monochromators are optical instruments, ordinarily used in connection with spectrophotometers (q.v.) and spectrofluorometers, (q.v.), which isolate

single wavelengths in ultraviolet, visible or infrared regions of the spectrum from the light provided by any source such as hydrogen, mercury, neon or xenon arcs. This

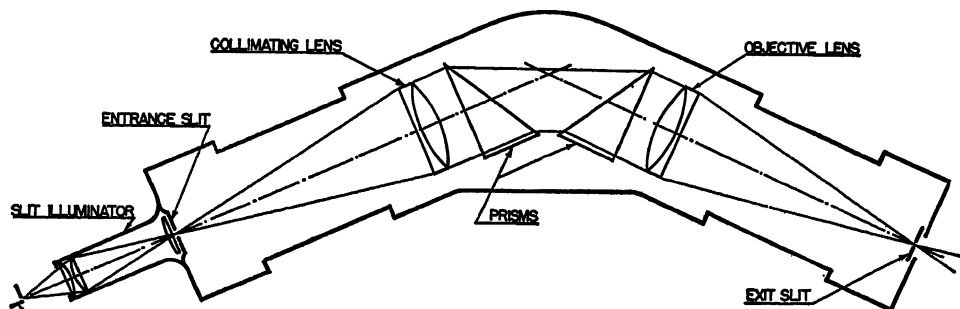


Fig. 1. Prism monochromator.

monochromatization is accomplished by the appropriate use of prisms for refraction or of ruled gratings for diffraction of the primary source into its spectrum. A typical optical system for a prism monochromator (Farand) is shown in Fig. 1. Light from the source is passed through an entrance slit and is then collimated by the first quartz-lithium fluoride achromat objective. The resultant

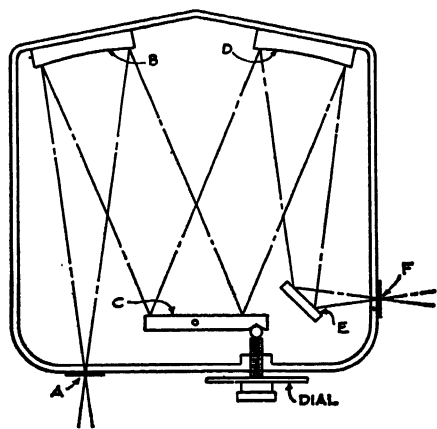


FIG. 2. Grating monochromator.

parallel radiation passes through the prism system where it is dispersed. The second objective images the entrance slit in the plane of the exit slit. The wavelength of the light issuing from the exit slit at a constant angle of deviation is varied by counter-rotation of the two 30° prisms to bring the desired wavelength into coincidence with the exit slit. The band width, or "spectral purity," transmitted at a given setting of the wavelength dial is controlled by the entrance and exit slit widths. Under normal conditions the band width is of the order of $1 \text{ m}\mu$ from 400 to $200 \text{ m}\mu$ or a spectral purity better than 90%.

The operation of grating monochromators is illustrated in Fig. 2. Light from a source is focused on entrance slit A and transmitted to a spherical mirror B, which reflects a parallel beam to grating C, dispersed and incident on spherical mirror D, then converged on plane mirror E to form the image which emerges through exit slit F. The grating monochromator is furnished to cover various ranges: 220–650 $\text{m}\mu$, 220–440 $\text{m}\mu$

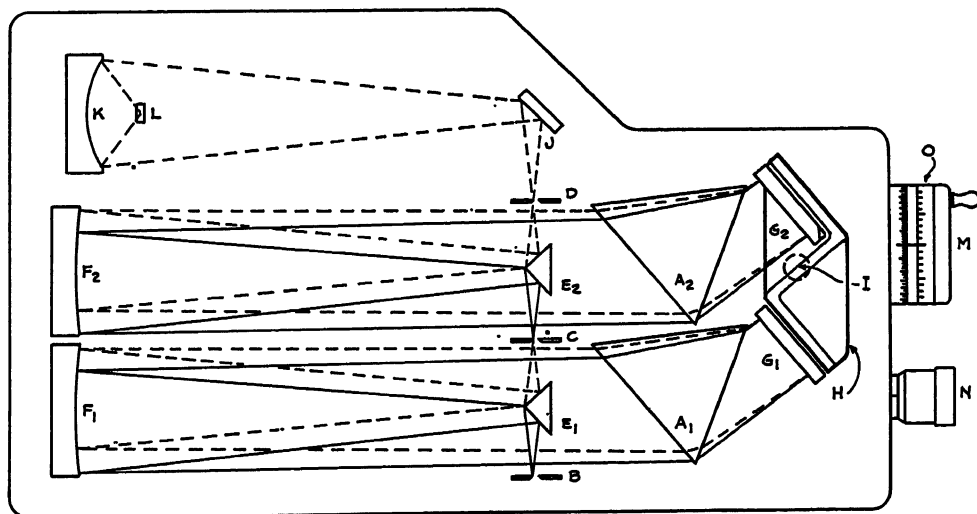


FIG. 3. Double monochromator utilizing prisms.

A₁ A₂ Prisms
B Entrance slit
C Center slit
D Exit slit
E₁ E₂ Newtonian mirrors

F₁ F₂ Collimating mirrors
G₁ G₂ Littrow mirrors
H Mirror turntable
I Center of rotation
J Plane mirror

K Ellipsoidal mirror
L Thermocouple position
M Wavelength control
N Slit width dial
O Wave scale

NEUTRON SPECTROMETRY

400–700 $m\mu$, 700–1400 or 2800 $m\mu$ (infrared), all identical except that they utilize differently blazed gratings.

The double monochromator utilizing prisms (Fig. 3) reduces scattered radiations to a negligible magnitude. Hence higher

spectral purity and greater resolution are provided. It is easily converted into a double spectrometer. Detailed information on construction and performance may be obtained from the manufacturers.

G. L. CLARK

NEUTRON SPECTROMETRY

ABSORPTIOMETRY

Just as spectrophotometry for ultraviolet, visible and infrared light, (q.v.) and x-ray absorptiometry (q.v.) are methods of chemical analysis, so also may the absorption of thermal neutrons be used for quantitative determination of various chemical elements. Again the simplicity of the apparatus required commends such an application, especially for those elements such as boron which have high neutron absorption cross sections. An excellent example of a few analyses which have been reported, mostly in Atomic Energy Commission reports, is the determination of boron by DeFord and Braman.¹ The sensitivity, precision and selectivity of the neutron absorption method depends largely on the geometrical arrangement of the neutron source, moderator, sample and detector. The optimum conditions are realized when the detector tube (BF_3 counter tube as described on page 663), is completely surrounded by the sample in solution, and both the neutron source and sample are imbedded in the moderator, which is a block of paraffin wax, typically 1 ft. square and 6 in. high. With such an arrangement the counting rate is 0.003 to 0.01 times the rate of production of neutrons by the small source, a 10 mc mixed radium-beryllium, thus permitting counting times of only a few minutes. The counting rate is then related to the concentration of boron by a simple mathematical equation. For a

sample containing about 1 g. boron a precision of $\pm 0.5\%$ is attained, or for very small amounts of boron about ± 1.0 mg. Separation of boron from other elements is not required since other elements associated in a compound have very low neutron absorption cross sections; because the method is based on a nuclear property the state of chemical combination is immaterial; and the method is entirely nondestructive. The most serious disadvantages are low sensitivity and comparatively large weight of sample required for highest possible precision. Conceivably the neutron spectrometer could be used here as a monochromator for the beam to be absorbed, with perhaps simplified calculations and interpretations. This of course would require an intense beam of neutrons from a reactor; but such as absorptiometer technique is inevitable.

REFERENCE

1. DEFORD, D. D. AND BRAMAN, R. S., *Anal. Chem.*, **30**, 1765 (1958).

G. L. CLARK

BASIC PRINCIPLES AND INSTRUMENTATION*

The Wave Nature of the Neutron

Although it is only in recent years, with the advent of chain-reacting atomic piles,

* Based in part on Chapter 1, "Neutron Diffraction," by G. E. Bacon; Oxford Univ. Press, 1955.

that neutron diffraction has become a subject of some importance in the study of the solid state, nevertheless it was shown as long ago as 1936 that neutrons could be diffracted. Elsasser (1936)¹ first suggested that the motion of neutrons would be determined by wave mechanics, so that they would be diffracted by crystalline materials and, shortly afterward, an experimental demonstration of this was given both by Halban and Preiswerk (1936)² and by Mitchell and Powers (1936).⁴ These experiments were done using a radium-beryllium neutron source, the neutrons from which were by no means of constant velocity, or "monochromatic," and, while sufficient to demonstrate that diffraction occurred, they were not of course sufficient to provide any quantitative data.

Neutron Beams from Atomic Piles

With the development of atomic piles, neutrons have been made available in sufficient numbers to allow collimation into beams and segregation in energy within a fairly narrow band. Thus there has grown up a technique of *neutron diffraction* on rather similar lines, but on a different scale, to the familiar technique of *x-ray diffraction* which developed from von Laue's classic discovery of 1912 that crystals would diffract x-rays. The first apparatus of this sort, usually termed a "neutron spectrometer," although it has been suggested that "diffractometer" would be more accurate, was built at the Argonne National Laboratory in 1945 (Zinn, 1947).⁵

If neutrons or any other radiation with wave properties are to be of use in investigating the arrangement of atoms in solids, it is necessary for their velocity to be such that they have a wavelength of the same order as the distance of separation of these atoms. This requirement accounts for the very general use of the x-radiation of copper of wavelength 1.54 Å by the x-ray crystallographer. In the case of neutrons the equivalent

wavelength λ is given, according to wave theory, by the equation

$$\lambda = h/mv, \quad (1)$$

where h is Planck's constant and m and v are the mass and velocity, respectively, of the neutrons. If we consider neutrons which have made a large number of collisions with atoms in an atomic pile at temperature T before being allowed to escape from the pile, then they will have a root-mean square velocity v appropriate to that temperature, and given by the equation

$$\frac{1}{2}mv^2 = \frac{3}{2}kT, \quad (2)$$

where k is Boltzmann's constant. From equations 1 and 2 it follows that

$$\lambda^2 = h^2/3mkT, \quad (3)$$

from which it can be shown that the wavelengths corresponding to the root-mean square velocities of neutrons in equilibrium at temperatures of 0° C and 100° C are 1.55 Å and 1.33 Å, respectively.

It is a fortunate circumstance that these wavelengths are of just the magnitude desired for the investigations of atomic arrangements, since it is neutrons having temperatures of this order which can be most conveniently obtained from an atomic pile. These neutrons will have been slowed down by making many collisions with a moderator of graphite or heavy water and will tend to come into thermal equilibrium at the pile temperature. They will have a distribution of velocities which follows a maxwellian curve appropriate to a temperature of the order of 100° C. By inserting a collimator into the pile face a beam of these neutrons can be extracted. The spectral curve shows the variation of counting rate, or number of neutrons counted per minute, in the beam diffracted by a single crystal of calcium fluoride set, successively, to reflect various wavelengths. It is clear that the spectrum is "white," resembling a beam of white x-rays *without* the superposition of any characteristic radiation.

The neutron beam from the pile impinges on a crystal which is amply large enough to receive the whole of the beam, and the counting rate is recorded for various values of θ . At any particular angle neutrons will be reflected into the counter if they lie within a small band of wavelength centered about a value λ , satisfying the Bragg equation

$$\lambda = 2d \sin \theta, \quad (4)$$

where d is the interplanar spacing of planes parallel to the crystal surface.

By suitable choice of the angle θ , a beam of neutrons of any desired wavelength can be separated out by the crystal and is then available for diffraction by a specimen placed in the position occupied by the counter. Actually, then, the neutron spectrometer operates principally as a monochromator.

In comparing the above method of producing a "monochromatic" neutron beam with the familiar use of a monochromator for producing crystal-reflected x-rays, an important difference must be emphasized. In the latter case the reflected radiation comprises solely a single line or close doublet of the x-ray spectrum, for example, the copper $K\alpha$ line, the monochromator separating this line from the general range of wavelengths which constitute the background of white radiation. In the neutron case there is no equivalent of the line spectrum and the monochromator merely selects a band of wavelengths. The width of this band of wavelengths is determined largely by the angle of divergence in the horizontal plane of the incident beam from the collimator. In practice this angle has to be relatively large, amounting to $\pm 1\frac{1}{2}^\circ$ in many cases, in order to give adequate counting rates, with the result that the wavelength band is of the order of 0.05 Å in width. This width is one of the factors which limits the resolution which can be obtained in the diffraction patterns, particularly at the larger values of the Bragg angle.

Neutron Spectrometers

It will be clear that, in principle, the production of a monochromatic beam of neutrons, as briefly described above, has similarities to the production of crystal-reflected x-rays; however, it is when the physical sizes of the two sets of apparatus are considered that it is realized that the details of the two diffraction techniques will be quite different. The intensity of the neutron beam which can be obtained from an atomic pile is greater by some orders of magnitude than that from a radium-beryllium source. Nevertheless, in comparison with the number of quanta in the x-ray beams from orthodox diffraction tubes, and the efficiency with which they can be detected, it is effectively a very weak beam. Consequently a beam of large cross-section has to be used, collimation can only be relatively poor, specimen dimensions are in inches rather than millimeters, and in place of the usual x-ray camera, which is some inches in diameter, we require the neutron spectrometer to be measured in feet. It is indeed fortunate that the absorption coefficients of most materials for neutrons are low, otherwise it would not be possible to use the large samples which are essential in order to give adequately large diffracted intensities. Massive shielding with borated paraffin, lead or cadmium is essential for protecting both the operator and the detecting apparatus from the main beam of neutrons and γ -radiation which emerges from the collimator. Only 1 per cent or so of this mixed radiation, namely, thermal neutrons having wavelengths within a narrow band, is reflected by the monochromator and subsequently used in the neutron diffraction measurements. Practically the whole of the emerging beam is undeviated by the monochromator and, unless steps were taken to prevent this, would undergo scattering by air molecules and any solid matter in its path.

Normally the neutron beam emerging

from the pile will have dimensions of the order of an inch square, in order to provide adequate diffracted intensities but without requiring the diffracting specimen and counter to be of impracticable size.

The diffracted neutrons from a known crystal analyzer (spectrometry), or a single crystal or powder undergoing analysis (diffractometry) are received in a counter which can be rotated about the center of the spectrometer. In the majority of the experimental work carried out so far this has been a proportional counter filled with boron trifluoride enriched in the boron isotope of mass 10. Such cylindrical counters have been described in detail by Fowler and Tunnicliffe (1950).² To obtain an adequate counting efficiency it is essential to use the highly absorbing boron isotope B¹⁰. Even then it is necessary to use a counter about 2 feet in length in order to get a counting efficiency as high as 80 per cent. The diameter of the counter must be about 2 inches in order to receive the diverging beam adequately. When a counter of this size is surrounded by a sufficient thickness of shielding material, consisting in practice of perhaps 4 inches of borated paraffin or layers of paraffin and boron carbide, the completed counter assembly weighs about 200 pounds. Consequently the conventional neutron spectrometer is not only large in dimensions but massive in construction.

In operation the counter arm of the spectrometer may be rotated manually or automatically at a very slow speed under the power of an electric motor. The method of counting will depend on the particular in-

vestigation. The counter impulses, after amplification and passage through a discriminating circuit which rejects the small pulses due to γ -radiation, may be fed to scaling units or to a ratemeter. In some cases point to point counting for a selected time interval may be carried out at successive positions of the counter arm, the individual counts being recorded by some automatic printing device. Alternatively, the counter arm may be rotated continuously and a ratemeter output fed to a pen recorder. In either case it is found in practice that the recording of the diffraction pattern has to be done very slowly: to record a pattern up to a Bragg angle θ of 45°, entailing a 90° travel of the counter arm, will usually occupy about 12 hours. The slow rate of recording is a consequence of the weakness of the diffracted peaks and the appreciable intensity of the background. At any point counting has to be carried out for a sufficient length of time for the statistical fluctuations in the rate of arrival of the neutrons at the counter not to be important.

REFERENCES

1. ELASSER, W. M., *Compt. rend., Acad. Sci. Paris*, **202**, 1029 (1936).
2. FOWLER, I. L. AND TUNNICLIFFE, P. R., *Rev. Sci. Inst.*, **21**, 734 (1950).
3. HALBAN, H. AND PREISWERK, P., *Compt. rend. Acad. Sci.*, **203**, 73 (1936).
4. MITCHELL, D. P. AND POWERS, P. N., *Phys. Rev.*, **50**, 486 (1931).
5. ZINN, W. H., *Phys. Rev.*, **71**, 752 (1947).

G. L. CLARK

NEUTRON ACTIVATION PRODUCTS ANALYSIS.
See GAMMA-RAY SPECTROMETRY, p. 377.

NUCLEAR MAGNETIC RESONANCE SPECTRA

ANALYTICAL APPLICATIONS

General Characteristics. The characteristics of nuclear magnetic resonance spectrometry (NMR) make it very well suited to the solution of certain analytical problems which can be solved only with difficulty, if at all, by other available analytical methods. The advantages of NMR for these preferred analytical problems are greater speed, greater certainty of identification of the functional groups, or greater ease of sample handling. The current and potential applications of this technique will be outlined in this article, with references to key literature articles which can provide the basis for further study.

NMR spectrometry is reasonably sensitive, in that a number of isotopes are measurable in concentrations of 1.0 % or less. Sensitivity varies with the magnetic properties of the isotope and, under some conditions, is limited by the isotope's environment. Liquid samples provide the best signals, although gaseous and solid samples are sometimes satisfactory for the most easily observable isotopes. The technique is not suitable for trace analysis where concentrations are in the ppm range.

The method is relatively fast, requiring 10–30 minutes per sample. This gives it a decided time advantage over the usually slower chemical methods, and in many cases a decided advantage over those physical methods which require either lengthy running times, such as gas chromatography, or lengthy and involved computation, such as mass spectrometry.

Good quantitative precision and accuracy are achieved when proper instrumentation is employed or when proper corrections are applied.⁹ For instance, with care, the total hydrogen content of a sample can be measured with a standard deviation of 0.2 wt. per

cent on the sample, at a level of 10 %, while relative hydrogen distribution (at high resolution) can be measured with a standard deviation of 5.0 % of the amount present as each type.

NMR spectrometry is non-destructive to the sample. This is very important where limited amounts of sample are available and it is desired to retain the sample for additional work. Furthermore, the normal sample container is a cylindrical glass tube which can be sealed. This means that materials which are highly reactive in the presence of air or water, or which are highly susceptible to contamination, can be sealed in inert atmospheres or under vacuum and can remain so sealed throughout the NMR study.

Wide Line Spectra. NMR spectrometry is usually divided into two categories, wide line and high resolution. Wide line spectra are those in which the observed width of the resonance line is as large or larger than the major resonance shifts caused by differences in the chemical environment of the observed nucleus. This type of spectrum gives information concerning the concentration and physical environment of the observed nucleus, but does not give information concerning its chemical environment. The wide line technique is applicable to all isotopes observable by NMR. It is applicable to solid, liquid, or gaseous samples, although liquids are usually preferable. Sample volumes required vary from about 0.1 to 50 cc, depending on the type of instrument used and the sensitivity needed.

The Larmor precession frequency, which is a function of the magnetic moment and spin quantum number of the isotope as well as a function of the magnetic field, is used to identify the isotope being observed. Ambiguities may arise in some cases, but in general this frequency is indicative of specific isotopes.

Under proper instrumental conditions the area under the absorption band is directly proportional to the number of atoms of the observed isotope in the effective sample volume. The proportionality constant varies with instrumental factors, but does not vary with the chemical or physical environment of the isotope. This means that quantitative measurements of the observable isotopes require calibration with only a single standard for each isotope, eliminating the need for determining absorptivities for individual compounds and individual environments. This gives NMR a marked advantage over the spectrometric techniques which do require the detailed absorptivity measurements.

Precision and accuracy of the NMR measurements are limited by those environmental factors which broaden the resonance excessively and thus seriously reduce the signal-to-noise ratio. Such broadening can be caused by severely restricted molecular motion, paramagnetic properties of the sample, electric quadrupolar effects, and critical collision frequencies. These adverse environments are encountered more frequently in solids and gases than in liquids.

Wide line NMR is potentially capable of determining the concentrations of a sizeable number of the elements. It is limited by the natural abundance and resonance characteristics of the observable isotope. In general, only those isotopes which contain odd numbers of protons in their nuclei are observable, but some exceptions, like beryllium, may have an even number of protons and an odd number of neutrons. Isotopes with even numbers of both protons and neutrons do not have magnetic moments and are not observable by this technique.

The width and shape of the resonance line may indicate the physical environment of the isotope. The multiplicity of spectral peaks resulting from dipole-dipole interaction in solids has been used to determine the arrangement of atoms in solids.^{1, Chap. 6}

The width of the resonance line is indicative of the degree of motional freedom of the isotope in the physical environment in which it is located.⁷ This is useful for determining the degree of "crystallinity" of polymers, for determining water or hydrocarbons adsorbed on solids, and for solving similar problems where there are wide differences in the degree of motional freedom of the observed atoms. An example of this is indicated in Figure 1 in which the appearance of the derivative wide line spectra of polyolefin samples of three different degrees of crystallinity are portrayed. Relatively free internal motion in sample A results in a relatively sharp resonance, while highly restricted internal motion in sample C results in a broad resonance. Materials which contain both relatively free and relatively restricted motional conformations produce the combined sharp and broad lines indicated in B. These can be resolved into measurements which indicate the relative percentages of the hydrogen atoms involved in the free and restricted rotational conformations.

Changes in motional freedom with changes in composition, temperature, pressure, and other environmental factors can also be studied by observing changes in line width and shape. Such data provide insight into the physical structure of polymeric materials, especially when combined with other measurements of the properties of these materials.

High Resolution Spectra. High resolution spectra are those in which the observed widths of the resonance lines are smaller than the major resonance shifts caused by differences in the chemical environment of the observed nucleus. This type of spectrum supplies unique information about the distribution of an isotope according to its chemical environment and is, therefore, of great importance in the determination of molecular structure.

The high resolution technique can be applied to only a limited number of isotopes.

NUCLEAR MAGNETIC RESONANCE SPECTRA

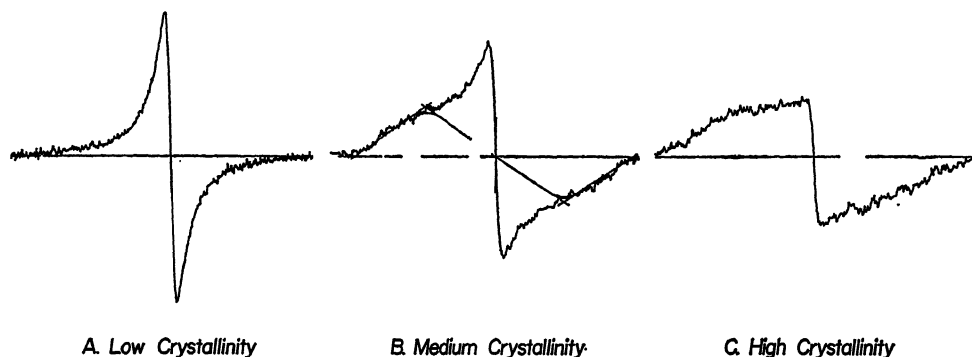


Fig. 1. Derivative wide line NMR spectra of olefin polymers of differing crystallinities. Determined by L. Westerman.

Those which have been observed successfully to date are H^1 , F^{19} , P^{31} , B^{11} , N^{14} , C^{13} , O^{17} , Si^{29} , Co^{59} , Pb^{207} .³ Isotopes which cannot be observed directly may often be observed indirectly by their effect on the resonances of observable isotopes with which they are intramolecularly associated. This is particularly true in the case of unobservable isotopes associated with H^1 .

An outstanding advantage of high resolution NMR is its simplified calibration requirements. As with wide line NMR, intensity calibration for individual compounds is unnecessary. If the relative concentrations of an isotope in various chemical environments is adequate information, it is not even necessary to determine the sensitivity of the instrument to the isotope being observed. Chemical shift calibration can be entirely indirect. This means that it is not necessary to use the precise compound being investigated for chemical shift calibration. It is only necessary to observe the functional groups of interest in any convenient compounds which may be available. These two factors are of tremendous importance in the investigation of the structure of compounds which have not been prepared before, or in the determination of the functional groups present in mixtures which cannot be separated for calibration purposes.

The sample volume required for high

resolution spectrometry is about 0.01–0.5 cc for the most important isotopes. This is somewhat larger than is required for gas chromatography, mass spectrometry, and some infrared observations, but is still reasonably small and makes the technique useful for observation of gas chromatographic cuts and other small samples. For practical purposes, the sample must be a liquid of low viscosity when observed, although gases can be observed with considerable sacrifice in signal-to-noise ratio. This means that solid materials must be liquified by melting or by solution in suitable solvents, and viscous liquids must be diluted or heated to reduce viscosity.

A typical high resolution NMR spectrum is presented in Figure 2. This spectrum is a recording of absorption amplitude *vs.* applied magnetic field strength at constant frequency. Strength of the applied magnetic field increases from left to right. This spectrum indicates the key features of high resolution spectra which are useful in the identification and quantitative determination of functional groups.

One of the most important features of high resolution spectra is the chemical shift, which is a function of the chemical environment of the observed nucleus. It is caused by secondary magnetic fields set up by several types of electronic currents induced into the

DETERMINED BY R.K. SAUNDERS

R_1 = RESONANCE OF HEXAMETHYL
DISILOXANE USED AS INTERNAL
STANDARD

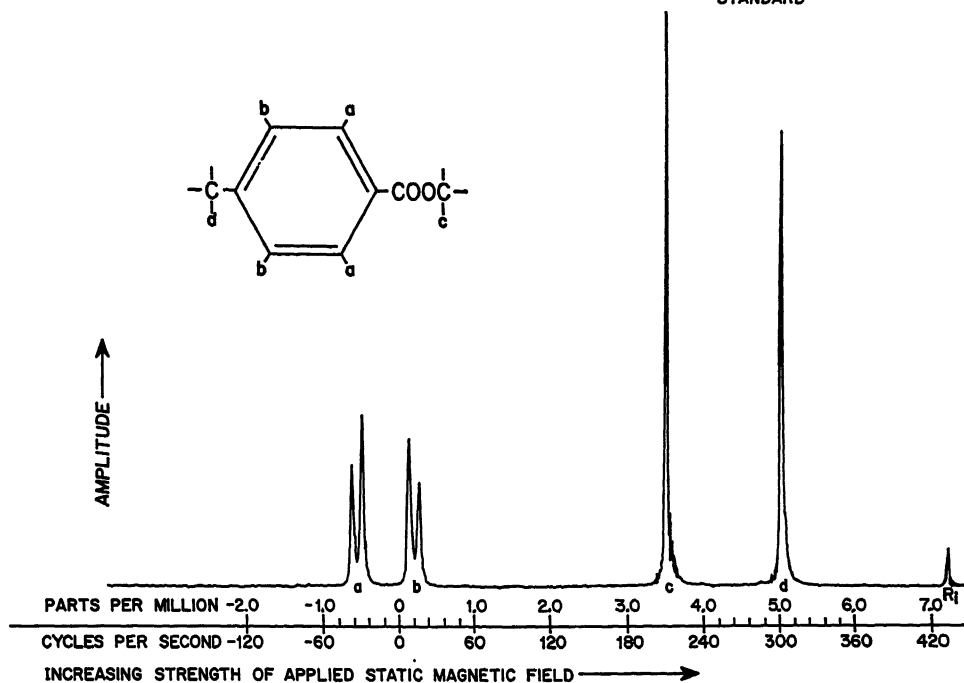


Fig. 2. High resolution H^1 spectrum of methyl *para*-toluate determined at 60 megacycles.

molecule by the applied magnetic field, and it is directly proportional to applied field strength. It is also proportional in part to the density of the electron cloud surrounding the observed nucleus. The chemical shift is measured from an arbitrary zero point which, in Figure 2, is the resonance position of benzene used as an internal standard. In order to make chemical shifts convertible from one frequency to another without change in values, the shifts are expressed in dimensionless units, such as the "parts per million" used for the upper scale of Figure 2. The chemical shift of a given resonance, then, is the displacement in terms of the dimensionless units from the resonance position of the reference material to the characteristic resonance position of the functional group of interest. The characteristic resonance position is that position which would be occupied by the resonance of the func-

tional group if it produced only a single peak. In Figure 2 hydrogen groups c and d produce only one peak each so that their chemical shifts are measured directly on the upper scale as 3.50 and 5.03 ppm, respectively. Measurement of the chemical shifts of the other two hydrogen types requires a detailed knowledge of the characteristics of the spin-spin multiplets produced.

A second key feature of high resolution NMR spectra is spin-spin multiplicity. This is caused by indirect coupling of nuclear magnetic moments through the bonding electrons. It is usually strongest in nuclei which are bonded together, and is attenuated rapidly with increasing numbers of bonds between nuclei. The number and the relative intensities of the peaks are functions of the number, the nuclear spin quantum number, and the ratio of coupling constant to chemical shift of the coupled nuclei.^{2, 4, 6}

These characteristics of spin-spin multiplets provide additional information concerning the spatial positions of the atoms in the molecule. In Figure 2, the pair of doublets produced by hydrogen types a and b indicate that these two types of protons are coupled together in pairs, and that the two pairs are identical.

The intensity of an entire resonance band, but not the intensities of the individual peaks within the band, is directly proportional to the number of atoms of the observed isotope in the effective sample volume when proper instrumentation and techniques are used or when proper corrections are applied.⁹ This makes it possible to determine the relative number of atoms of the observed isotope which are present in each of the observed chemical environments.

High Resolution NMR of H^1 . H^1 is the most important and most extensively studied isotope for a number of reasons. It is the most easily detected stable isotope observed (only H^2 has higher NMR sensitivity). Its chemical shifts and its spin-spin couplings follow regular and predictable patterns, and it is possible to associate a given functional group with a relatively narrow region of the

total H^1 chemical shift spectrum. This makes it possible to identify hydrogen-containing functional groups with a minimum of ambiguity and uncertainty. Since hydrogen occurs in most organic compounds, the resonance of this isotope is useful for the study of most organic compounds. On the debit side, H^1 has the smallest range of chemical shifts (about 15 ppm), which requires the highest quality of equipment and the highest operating skill. The resonance lines are usually sharp except when motion is restricted, but the small chemical shift frequently prevents complete resolution, and makes interpretation and quantitative measurement more difficult.

Perhaps the most obvious use for H^1 NMR spectra is the determination of functional groups present in and the structure of hydrogen-containing molecules. A prerequisite to this type of work is detailed data correlating hydrogen-containing functional groups with chemical shift. These data may be presented in a shift chart such as shown in Figure 3. Data of this type for a wide variety of hydrocarbons and their derivatives have been published.^{4, 8} Detailed discussions of the application of high resolution NMR

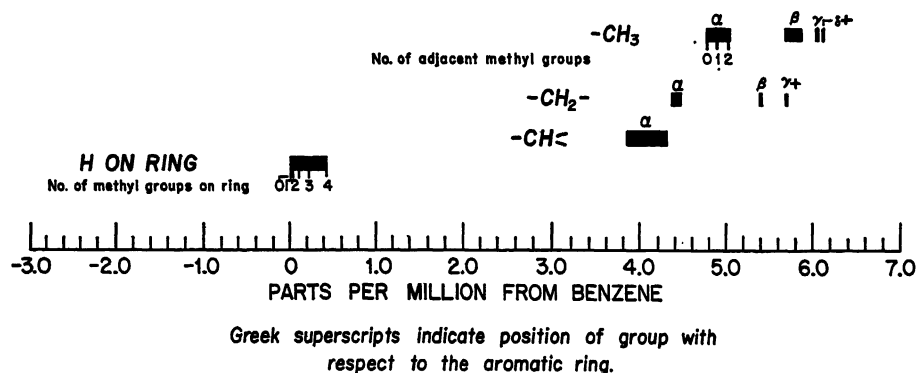


FIG. 3. Hydrogen magnetic resonance chemical shifts of alkyl benzenes.

spectra to the determination of molecular structure are also available.^{4, 6} NMR does not replace any of the other spectrometric methods in this work, but rather supplies unique and complementary information which makes possible positive identification of functional groups or of structural features which would not otherwise be possible at present. It also speeds up the identification of functional groups which can be determined only with difficulty by other methods. Thus it is a very valuable addition to spectrometric techniques.

Identification and quantitative measurement of hydrogen-containing functional groups can be made for mixtures as well as for pure compounds. This permits study of changes in the nature and concentrations of functional groups in mixtures. It sometimes makes it possible to determine quantitatively the amounts of individual compounds present, giving a complete multicomponent analysis of the mixture.^{5, 10}

Another type of analysis of mixtures, characterization, is intermediate between qualitative functional group identification and complete multicomponent analysis.¹¹ Characterization leads to the determination of the structure of the average molecule in the mixture, and gives one an insight into the types of reactions which may have led to this kind of structure and to the uses to which such a mixture might be put. Characterizations of alkyl aromatics can determine the average number of aromatic rings per molecule and the average number, length, and branchiness of the alkyl chains. Such information can often be of vital importance in the study of aromatic fractions for which determination of individual components is difficult. For mixtures of olefins, characterization determines the relative amounts of hydrogen on the olefinic carbons and on the non-olefinic carbons. This can sometimes be interpreted as the average number of double bonds per alkyl chain, and

at times will indicate the relative amounts of terminal and non-terminal olefins present in the sample. For mixtures of saturates, characterization determines the ratio of methyl to non-methyl hydrogens. This leads to a value of the average molecular weight of normal paraffins, and to a measure of the branchiness of branched chain paraffins. Branchiness has been found to be correlatable with naphthene ring content and viscosity index of petroleum fractions.

Kinetic studies involving the appearance or disappearance of key functional groups are obviously relatively easy to perform, and since they can be performed in sealed tubes, it is easy to insure that the materials being studied do not become contaminated and do not lose any components by vaporization during the course of the study. The kinetics and thermodynamics of hydrogen bonding and exchange reactions and intramolecular rotational phenomena can be studied quite readily by NMR.⁶ In such cases it is usually necessary to study the changes in the NMR spectra with temperature.

Other Isotopes. Another isotope which has been extensively and successfully studied by high resolution NMR spectrometry is F^{19} . The resonance of this isotope can potentially supply the same kinds of information as that derived from H^1 resonance, but interpretation of the F^{19} spectra is more difficult. It is expected that interpretation difficulties will be reduced as more data become available, and that F^{19} resonance will play an important part in the study of fluorine-containing compounds. The resonance of P^{31} has also been studied and found to be quite valuable for the study of phosphorus compounds. The resonance of B^{11} , although not extensively studied to date, appears to be quite useful for the determination of the structure of boron compounds, particularly the boranes. The resonances of N^{14} , N^{15} , C^{13} , O^{17} , Si^{29} , Co^{59} , and Pb^{207} have not been studied extensively to date, either because their

usefulness is limited by low natural abundance or by difficulty of observation, or because there simply has not been much demand for the information that these resonances can supply. There are other isotopes which can be observed by NMR, but it has not yet been reported whether any more of these isotopes can be observed by high resolution. It is expected that additional useful isotopes will be studied in the future. A comprehensive review of the high resolution NMR data from all isotopes studied so far has been published by Brownstein.³

REFERENCES

1. ANDREW, E. R., "Nuclear Magnetic Resonance," Cambridge University Press, London (1956).
2. BERNSTEIN, H. J., POPLER, J. A., AND SCHNEIDER, W. G., *Can. J. Chem.*, **35**, 65 (1957); **35**, 1060 (1957).
3. BROWNSTEIN, S., *Chem. Rev.*, **59**, 463 (1959).
4. CHAMBERLAIN, N. F., *Anal. Chem.*, **31**, 56 (1959).
5. CHAMBERLAIN, N. F., NEUREITER, N. P., SAUNDERS, R. K., AND WILLIAMS, R. B., Proceedings of the Fifth World Petroleum Congress, Section V, Paper No. 8 (1959).
6. ROBERTS, JOHN D., "Nuclear Magnetic Resonance," McGraw-Hill, New York (1959).
7. SLICHTER, W. P., *Advances in Polymer Science*, **1**, 35 (1958); Bell Telephone Tech. Pub. Monograph 3049.
8. TIERS, G. V. D., *J. Chem. and Eng. Data*, in press.
9. WILLIAMS, R. B., *Ann. N. Y. Acad. Sci.*, **70**, 890 (1958).
10. WILLIAMS, R. B., "Proceedings of the Conference on Molecular Spectroscopy," Pergamon Press, London (1959); *Spectrochim. Acta*, **XIV**, 24 (1959).
11. WILLIAMS, R. B., ASTM Special Tech. Pub. No. 224, 168 (1958).

In addition to references 1, 3, and 6, the following books, which were published after this article was written, contain comprehensive discussions of the theory and applications of NMR:

1. JACKMAN, L. M., "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York (1959).
2. POPLER, J. A., SCHNEIDER, W. G., AND BERN-

STEIN, H. J., "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York (1959).

NUGENT F. CHAMBERLAIN

INSTRUMENTATION AND THEORY.*

When atomic nuclei for which the proton, H^1 is simplest and best known example, are placed in a constant magnetic field of high intensity and subjected at the same time to a radio-frequency alternating field, a transfer of energy takes place between the high-frequency field and the nucleus to produce a phenomenon known only since 1946 as *nuclear magnetic resonance* (NMR). The discovery, made simultaneously for protons by Edward Purcell and associates (9) at Harvard University and Felix Bloch and associates (4) at Stanford University was recognized by award of the Nobel prize in physics jointly in 1952. Spectra due to NMR result from many atomic nuclei having spin angular momentum, characterized by a quantum number $I = n/2$, where n is 0 or an integer which must be determined for a given nucleus. The circulation of positive charge associated with the spin of the nucleus causes it to possess a magnetic moment directed along its axis of spin expressed by $g\beta[I(I + 1)]^{1/2}$, where β is the nuclear magneton and g is a nuclear factor found by experiment.

If a nucleus is placed in a uniform magnetic field, H_0 , it experiences a torque, with the result that it precesses about the applied field, analogous to the precession of a gyroscope spinning in the earth's gravitational field. The component of magnetic moment in the direction of H_0 is quantized, so that the various energy levels correspond to different orientations of the nuclear magnet with respect to H_0 . The maximum allowed component of magnetic moment is disig-

* Abridged from an article by the same author in "Encyclopedia of Chemistry Supplement," Reinhold, N. Y., 1958, p. 198.

nated μ , the magnetic moment of the nucleus.

If a system of nuclei in a magnetic field is exposed to radiation of frequency ν_0 such that the energy of a quantum of radiation, $h\nu_0$, is exactly equal to the energy difference between two adjacent nuclear energy levels, then energy transitions may occur in which the nuclei may be pictured as flipping back and forth from one allowed orientation to another. A quantum of energy is equally likely to tip a nucleus in either direction, so that there is a net absorption of energy from the radiation only when the number of nuclei in one energy level exceeds the number in another, as would occur if the nuclei were in thermal equilibrium with surroundings according to a Boltzmann distribution.

Under these conditions a nuclear magnetic resonance spectrum is observed, the lines corresponding to energies required to flip the nuclei among allowed orientations in the magnetic field. The radiation required lies in the radio-frequency region at frequencies of the order of 100 kilocycles to 40 megacycles (wave lengths 3000 and 7.5 meters, respectively). For example, for protons in a magnetic field of 10,000 gauss, radiation of 42.6 Mc/sec is required. As there is a linear relation between the resonance frequency, ν_0 , and the magnetic field H_0 , NMR spectra may be expressed as intensity of absorption plotted against ν_0 at fixed H_0 or against H_0 at fixed ν_0 . Generally the resonance of a substance is measured in terms of the precession speed at which the nuclei flip over. Instead of tuning into the resonance by varying the frequency of the rotating magnetic field, the frequency is fixed and the main magnetic field which controls precession speed is varied; when the nuclei flip the resonance reading is taken as the strength of the magnetic field in gauss or oersteds at that point.

The apparatus for NMR experiments is relatively simple and comprises a large magnet and electronic equipment to generate rf

radiation and to measure its absorption by the sample. A simplified block diagram is shown in Fig. 1. Excellent commercial NMR apparatus is now available. A surprisingly large and growing list of applications of NMR can be only briefly indicated. Analytical applications are ably discussed in the companion article by N. F. Chamberlain.

(1) *Fundamental measurements of nuclear moments.* Complications and interactions which may limit the accuracy of measurement actually lead to other valuable applications as noted later.

(2) *The location of hydrogen atoms in solids.* A solid containing pairs of hydrogen nuclei such as a salt hydrate will give a resonance spectrum in the form of a doublet,

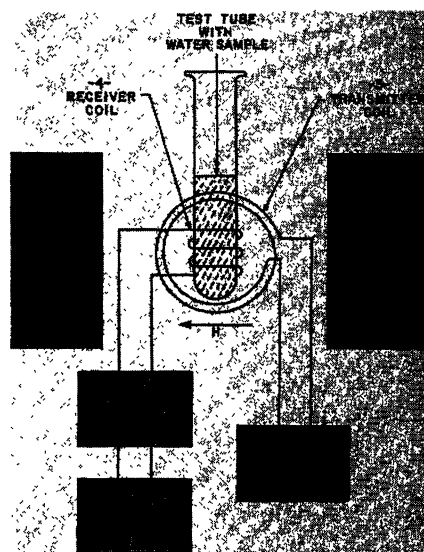


FIG. 1. 1. A magnet in which the gap field H can be changed from zero up to, say 10,000 gauss; 2. low-power radio transmitter which supplies r-f energy to 3. a small transmitter coil placed in the magnet gap as shown; 4. a small receiver coil which is located within the transmitter coil and which surrounds 5. a "Pyrex" test tube containing a sample of ordinary water; 6. a sensitive radio receiver (tuned to the same frequency as the transmitter) and capable of amplifying any signal which might be induced in the receiver coil, and 7. an indicator such as a graphic recorder, oscillograph or voltmeter, which can register the presence of such signals.

corresponding to effective magnetic fields $H_0 + H_{100}$ and $H_0 - H_{100}$ (where H_{100} is the weak local magnetic field generated by a hydrogen nucleus). A triangular configuration of nuclei with 3 peaks, tetrahedral with flat-topped curves, etc. indicates that the shape of the spectral curve can be used to identify nuclear configurations, and the internuclear distances, especially useful for hydrogen atoms which cannot be located by x-ray diffraction analysis for example.

(3) *The type of bond—ionic or non-ionic in the solid state.* This is illustrated by boron trifluoride dihydrate which in the liquid state is ionized about 20% according to $\text{BF}_3 \cdot 2\text{H}_2\text{O} \rightleftharpoons [\text{BF}_3\text{OH}]^- + \text{H}_3\text{O}^+$. As crystals the NMR spectrum would display a doublet if non-ionized for the pair of protons in the water and a triplet for the ionized state with an intense central maximum due to the isolated hydrogen in $[\text{BF}_3\text{OH}]^-$ ion. The first is found to be true; the opposite is true (completely ionic) for crystalline $\text{HNO}_3 \cdot \text{H}_2\text{O}$. In glasses of both compounds formed by rapid cooling of the liquids, both non-ionized and ionized molecules are found.

(4) *Bond lengths.* The mean square width of the absorption curves is related to the sum of the inverse sixth powers of the internuclear distances in the crystal. This has made it possible to measure bond lengths to hydrogen in NH_4^+ , PH_4^+ , BH_4^- and NH_2^- , and hydrogen bonds in HF_2^- , hydrazine fluoride, and other cases.

(5) *Quadrupole interactions.* Nuclei with spin quantum numbers greater than $\frac{1}{2}$ possess usually an electric quadrupole moment as well as a magnetic dipole moment, arising from aspherical distribution of positive charge over the nucleus (oblate or prolate spheroid). The result may be several absorption lines instead of only one, the separation between the nuclear resonance lines permitting calculation of the quadrupole interaction as the product of the electric field gradient at the nucleus and the nuclear electric quadrupole moment. Measurements

have given very detailed information about some crystal structures.

(6) *Crystal imperfections and strain.* The quadrupole interaction energy just mentioned is zero in perfect cubic crystals where there is no electric-field gradient. But this symmetry is disturbed by imperfections and mechanical strains, so that the resulting broadening or splitting of nuclear resonance lines is an extremely sensitive measure of such effects.

(7) *Molecular motion in solids.* Widths and shapes of absorption lines in NMR spectra are dependent on temperature, indicative of hindered reorientation among a number of stable positions. Information is also derived from the spin lattice relaxation time, T_1 , of the nucleus, defined as the time required for a nucleus to exchange a quantum of energy with its immediate surroundings; the lifetimes of nuclei, T_1 , in a given level vary enormously from 10^{-4} second to many hours, the minimum, T_1 , occurring at a temperature at which the spectrum of frequencies of molecular motion is distributed with maximum intensity near the nuclear resonance frequency. From the observed change in T_1 with temperature, it has been proved that in crystalline benzene, the molecules undergo hindered reorientation about a hexane axis. Self-diffusion may narrow the line and reduce T_1 , as in cyclohexane and the alkali metals.

(8) *Quantitative evaluation of liquid components in solid-liquid mixtures.* When a solid is melted or dissolved, the molecular motion in the liquid is so vigorous as to even out all broadening interactions, so that very narrow lines are characteristic of the liquid state. In a spectrum of a superposed sharp line for liquid and broad line for the solid, it is easy to measure the intensity of the narrow component and thus to analyze quantitatively, for example, the amount of moisture in solid materials and the relative amounts of ordered or crystalline and of disordered or amorphous fractions in

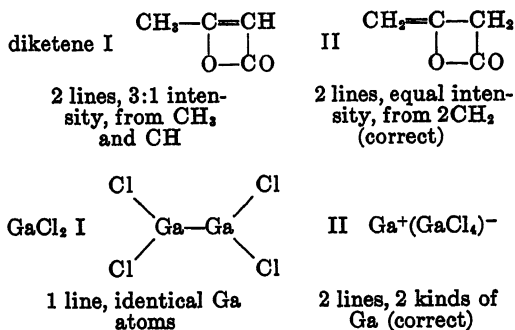
polymers (cf. Chamberlain article). The variation in line breadths, and of relaxation time as affected by liquid viscosity, or molecular changes, provide a useful but as yet little used method of studying the structures of liquids and solutions.

(9) *Chemical shifts and identification of functional groups in molecules.* The frequency ν_0 at which a nuclear resonance line occurs is governed by the equation $h\nu_0 = \mu H_0/I$, where μ is the nuclear magnetic moment, I the spin quantum number, and H_0 is the magnetic field actually experienced by the nucleus, which differs from the applied field H_{appl} by the equation

$$H_0 = H_{\text{appl}} (1 - a + b) = H_{\text{appl}} (1 - c),$$

where a is a diamagnetism induced by H_{appl} in molecular electrons, and is thus subtractive; b is a weak uncoupling of paired valence electrons to produce a paramagnetic moment and thus is additive; and c is the resultant combination whose value varies critically with particular electron distributions or chemical environments of the nucleus.

Ethyl alcohol, $\text{CH}_3\text{—CH}_2\text{—OH}$, has 3 proton resonance lines having intensities 3:2:1 corresponding to the number of protons in the three groups. Thus the characteristic positions of resonance lines are referred to in terms of chemical shifts, which are expressed as a fraction of the field by which resonance is shifted from some arbitrary standard, and which are directly related to the functional groups in which protons occurs. Thus groupings can be identified and relative numbers determined from intensities. For protons the shifts are a few parts per million, but for other nuclei such as cobalt the shift may be 1%. This is of course the application now being widely exploited in organic chemistry. Other examples of unambiguous choice between two alternative structures are:



(10) *Relative positions of groups in molecules from multiplet structures.* High resolution shows a fine structure of the 3 proton resonance lines of ethyl alcohol mentioned above. This multiplet interaction arising from the induction of weak uncoupling of paired valence electrons is even shown by HD for which the deuteron resonance line is a doublet and the proton line a triplet, reflecting the number of orientations which the nuclei adjacent to a given nucleus can assume. In alcohol, there are three combinations of $\text{—CH}_2\text{—}$ protons which $\text{CH}_3\text{—}$ may "see" and thus produce a triplet, and $\text{—CH}_2\text{—}$ experiences fields corresponding to 4 ways of arranging spins in CH_3 , and thus produce 4 lines. Thus it is not difficult to understand why NMR is a powerful tool, especially for the organic chemist.

(11) *Measuring the earth's magnetic field.* If very sharp precision in the strength of an applied magnetic field is needed to hit the resonance of a liquid compound, it should be possible to reverse the procedure and use resonance for precise measurement of magnetic fields, especially the earth's field. The difficulty here is that it is extremely weak, of the order of half a gauss. To measure this by a resonance phenomenon previously studied in the laboratory with fields of thousands of gauss posed a challenge which was solved by Varian and Packard with an ingenious instrument. This first lines up protons in a sample of liquid with a moderately weak magnetic field, so that the sample itself is a weak magnet. The polarizing field

NUCLEAR MAGNETIC RESONANCE SPECTRA

is suddenly switched off (as Pake describes it, the magnetic rug is pulled out from under the group of protons). The nuclear magnets, which have been lined up in a direction not parallel to the earth's field, now begin to precess around the axis of this field. Their alignment rapidly breaks down, but in liquid benzene it lasts up to 20 seconds, long enough to measure the strength of the earth's magnetic field to an accuracy of 1 part in 10 million, simply by tuning in on the precession rate of the group of protons; for since the earth's field produces the precession the rate is a measure of the strength of this field. The Varian-Packard instrument is called the proton precessional magnetometer. It is already in use for mineral deposit prospecting from helicopters; shot in rockets to measure the earth's field of various heights above the surface; and will be part of the instrumentation in artificial satellites.

REFERENCES

Books:

ANDREWS, E. R., "Nuclear Magnetic Resonance," Cambridge University Press, London (1956).

ROBERTS, JOHN D., "Nuclear Magnetic Resonance," McGraw-Hill, N. Y., (1959).

Semi-Popular articles and reviews:

PAKE, GEORGE E., *Sci. Am.*, 200 (Aug. 1958).

RICHARDS, R. E., *Endeavour*, 16, 185 (1957).

SHOOLERY, J. N. AND WEAVER, H. E., *Ann. Rev. Phys. Chem.*, Ch. 6, 433 (1955).

Varian Associates, Technical Inf. Bulletins, Vols. 1, 2 (1953-59).

Representative Research Papers:

1. ANDERSON, W. AND MCCONNELL, H. M., *J. Chem. Phys.*, 26, 1496 (1957), (mathematical analysis).

2. BECKER, E. D. AND LIDDEL, U., *J. Mol. Spect.*, 2, 1 (1958) (H bonding in ethanol).
3. BELL, W. E. AND BLOOM, A. L., *Phys. Rev.*, 107, 1559 (1957) (alkali metal vapor).
4. BLOCH, F., HANSEN, W. W., AND PACKARD, M. E., *Phys. Rev.*, 69, 127 (1946) (original discovery).
5. CALLIS, C. F., VAN WAZER, J. R., AND SHOOLERY, J. N., *Anal. Chem.*, 28, 269 (1956); *J. Am. Chem. Soc.*, 79, 2719 (1957) (phosphorus compounds).
6. MCCONNELL, H. M. AND WEAVER, H. E., *J. Chem. Phys.*, 25, 307 (1956) (cuprous-cupric solutions).
7. PIETTE, L. H., AND WEAVER, H. E., *J. Chem. Phys.*, 28, 735 (1958) (chemical shifts of Pb²⁰⁷).
8. PROCTOR, W. G., *Z. Anal. Chem.*, 164, 127 (1958) (chemical analysis).
9. PURCELL, E. M., POUND, R. V., AND TORREY, H. C., *Phys. Rev.*, 69, 37 (1946) (original discovery).
10. RAY, J. D., PIETTE, L. H., AND HOLLIS, D. P., *J. Chem. Phys.*, 29, 1022 (1958) (structural isomer discrimination).
11. REMPEL, R. C., WEAVER, H. E., SANDS, R. H., AND MILLER, R. L., *J. App. Phys.*, 23, 1082 (polyethylene).
12. SCHAEFFER, R., SHOOLERY, R. N., AND JONES, R., *J. Am. Chem. Soc.*, 80, 2670 (1958) (boranes).
13. SHOOLERY, J. N., *Faraday Soc. Disc.* 1955, No. 19, 215 (molecular structures).
14. SHOOLERY, J. N., *Svensk Kem. Tidsk.*, 69, 185 (1957) (chemical applications).
15. SHOOLERY, J. N. AND ROBERTS, J. D., *Rev. Sci. Inst.* 28, 61 (1957) (high temperature).
16. SHOOLERY, J. N., AND ROGERS, M. T., *J. Am. Chem. Soc.*, 80, 5121 (1958) (steroids).
17. WILLIAMS, R. B., *ASTM Tech. Publ.* 224, 168 (1953) (hydrocarbons in petroleum).

G. L. CLARK

RAMAN SPECTROSCOPY

APPLICATIONS

When a beam of essentially monochromatic radiation is scattered by a sample which does not absorb at the wavelength of the beam, the spectrum of the scattered radiation includes a line at this wavelength and also a number of relatively weak lines (or bands) at other wavelengths. These modified lines constitute the Raman spectrum of the sample.

The origin of Raman spectra can best be understood from a quantum theory point of view in which a beam of radiation is considered to be a stream of photons. These photons make collisions with the molecules in the sample. Most of the collisions are elastic; i.e., there is no exchange of energy and the only effect is a change in the photon's direction of travel. A small fraction of the collisions are inelastic with a photon either giving up some of its energy to a molecule or, if the molecule is already excited, taking some energy from the molecule and leaving it in its ground or lowest energy level.

The photons which have gained some energy have a higher frequency and a shorter wavelength than the incident photons. The corresponding part of the Raman spectrum is of little importance to applications and nothing further will be said about it here.

In a collision in which energy is transferred from a photon to a molecule, the molecule can accept only that amount of energy which will enable it to make a transition from its lowest energy level to a permitted excited level. The type of energy level which is most important here is the vibrational level which depends on the vibrational motions of atoms in the molecules.

Because the energy of a photon is proportional to its frequency, the difference between the frequencies of the incident and modified photons is proportional to the vibrational energy taken up by the mole-

cules. In the spectral region used for Raman spectroscopy frequencies cannot be measured directly, but wavelengths can be readily measured. The frequency difference is given by

$$\Delta\nu = \frac{c}{\lambda_i} - \frac{c}{\lambda_R}$$

in which λ_i and λ_R represent the wavelengths of the incident and Raman lines, respectively, and c is the velocity of light (3×10^{10} cm/sec). It is convenient and customary to use instead of frequency (number of waves per second) the wavenumber (number of waves per centimeter) which is obtained by dividing the frequency by the velocity of light. Thus,

$$\Delta\omega = \frac{\Delta\nu}{c} = \frac{1}{\lambda_i} - \frac{1}{\lambda_R} \quad (\text{in cm}^{-1})$$

The quantity $\Delta\omega$, which is known as the Raman shift or Raman frequency, is independent of the incident wavelength and is a property of the molecule responsible for the corresponding Raman line.

The Raman spectrum of a sample, which is the set of $\Delta\omega$ values observed, provides information about the vibrational energy levels of the molecules in the sample. This information is closely related to the information obtainable from the infrared absorption spectrum of the sample which is also the result of transitions between vibrational energy levels (rotational transitions are neglected here).

In general (and particularly for molecules of high symmetry) not all of the modes of molecular vibration result in Raman lines. Similarly not all modes of vibration result in infrared absorption bands. Because of the difference in the phenomena of scattering and absorption, a mode of vibration which is not "active" in Raman scattering may be active in infrared absorption and vice versa.

Consequently, although the data on vibrational energy levels supplied by Raman spectroscopy may partially overlap the data from infrared absorption spectroscopy, the two techniques supplement each other. To obtain a complete set of vibrational energy levels it is usually necessary to use both techniques. (For some molecules there are modes of vibration which are active in neither the Raman spectrum nor the infrared absorption spectrum).

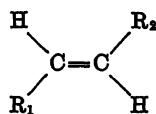
As might be anticipated from the above brief discussion, the applications of Raman spectra parallel those of infrared spectra. The major applications, with a short and over-simplified description of each, are as follows:

(1) **Determination of Molecular Structure.** When a plausible model for a not-too-complicated molecule is examined it is possible to predict theoretically the numbers of Raman lines and infrared absorption bands it should have. If the predicted numbers are significantly different from those observed, the model is unsatisfactory and it is discarded. When agreement is reached for some model, some of the observed Raman and infrared frequencies can be used in a theoretical treatment to calculate other vibrational frequencies. If there is agreement between the calculated and observed frequencies the model is a good representation of the molecule and the relative positions of the atoms in the molecule are known. At the same time information is obtained about the magnitude of the forces holding the atoms together in the molecule and conclusions can be drawn about the chemical bonds in the molecule.

(2) **Calculation of Thermodynamic Quantities.** By means of statistical mechanics it is possible to relate the values of such quantities as heat capacities, entropies, free energies of formation and equilibrium constants to molecular vibration frequencies. Even if the theoretical problem described in (1) is not completely solved, the set of fre-

quencies obtained from a combination of infrared and Raman spectra can often be used to calculate thermodynamic quantities, sometimes more accurately than they can be measured directly. In this way it is possible to calculate the equilibrium constant for a reaction which has never been carried out in the laboratory.

(3) **Determination of Functional Groups.** Correlations exist between the presence of certain functional groups in a molecule and Raman lines at certain frequencies which are quite similar to the well-known correlations of functional groups and infrared absorption bands. In many cases these correlations involve the same frequencies in both techniques; in some cases a correlation is unique for either Raman or infrared spectroscopy. For example, the presence of a carbonyl group in a saturated ketone is indicated by either a Raman line or an infrared band with a frequency (more accurately, wavenumber) near 1720 cm^{-1} and both techniques will give the same value to within a few reciprocal centimeters. Internal double bonds in trans-olefinic hydrocarbons represented by the formula



have a strong Raman line near 1675 cm^{-1} but the corresponding infrared band is absent or very weak. On the other hand, a useful infrared band at 720 cm^{-1} , which indicates the presence of four or more methylene groups in a chain, does not have a counterpart in the Raman spectrum.

(4) **Qualitative Analysis of Mixtures.** The Raman spectrum of a mixture whose components do not interact with other is a superposition of the Raman spectra of the components. Because the set of vibrational energy levels is unique for each kind of molecule, a qualitative analysis of a mixture can be carried out by comparing the Raman spectrum of the mixture with the spectra of

the pure compounds which might be present in the mixture. When all of the strong Raman lines of a pure compound are found in the spectrum of a mixture and the relative intensities are the same in the two cases, it can be concluded that the compound is present in the mixture. In applying this method of qualitative analysis it is desirable to have mixtures which are not so complicated that extensive overlapping of Raman lines from different compounds occurs. The number of components which can be present depends on their nature; it is seldom possible to make reliable analyses with more than six components. Auxiliary information about the sample can often improve the reliability of an analysis, as in the analogous application of infrared spectra.

(5) Quantitative Analysis of Mixtures.

If there is no interaction between the components in a mixture, the intensity of each Raman line of any component is proportional to the concentration of that component in the mixture provided that the Raman line is not overlapped by lines from other components. This is the basis of quantitative analysis by means of Raman spectroscopy. For calibration a sample of each of the compounds to be determined is usually sufficient, although it is advisable to check the calibration with some mixtures of known composition in the concentration ranges of interest. If several unoverlapped Raman lines are available for a component, one can make independent determinations from each line and thus obtain internal checks on the accuracy of the analysis. Although in principle it would be possible to use overlapped lines for analysis, in practice it is preferable to avoid this by restricting the number of components present with the use of some method of fractionation.

In some cases a complicated sample may include a number of components of the same chemical type with a functional group in common. The position of the Raman line related to this functional group would, in gen-

eral, vary slightly with changes in the rest of the molecule. If the total concentration of compounds of the same chemical type is desired, this can be obtained by integrating the intensity over the small spectral range which includes the possible positions for the characteristic Raman line. The method of calibration of such a group or type analysis depends on the nature of the sample and the analytical accuracy needed. It is often true that the intensity of a characteristic Raman line is not sensitive to changes in the rest of the molecule. In that event the calibration can be based on the spectra of a limited number of representative compounds. Sometimes a separation method can be used to segregate the compounds in the desired class and such samples can be used for calibration.

Advantages and Disadvantages of Analytical Applications

In applications (1) and (2) above, the use of Raman spectroscopy is essential. In analytical applications, however, there usually are alternative methods and it is appropriate to consider those features which might make the use of Raman spectroscopy desirable or undesirable in individual cases. A discussion of these features is complicated by the fact that some of the limitations which have been experienced in the past are due more to inadequacies of instrumentation than to anything more fundamental. Only relatively recently has satisfactory apparatus for Raman spectroscopy become commercially available.

The advantages of Raman spectroscopy may be summarized as follows:

(1) The Raman spectrum of a compound is a relatively simple pattern of lines, some of which may be quite sharp while others are broad and diffuse.

(2) The complete range of vibrational frequencies can be covered with one instrument.

(3) The sample container (Raman tube) is made of glass.

RAMAN SPECTROSCOPY

(4) Water as a solvent presents no problem because the Raman spectrum of water is diffuse and weak.

(5) The linear relationship between Raman line intensity and concentration makes the calculations involved in quantitative analysis extremely simple.

(6) Integration over a portion of the Raman spectrum is relatively simple.

The disadvantages of Raman spectroscopy are:

(1) An analytical sample is practically limited to a clear, colorless (non-absorbing) liquid. Although Raman spectra can be obtained for solid, gaseous, or (with some limitations) colored samples, the problems involved make analytical applications impractical for such samples.

(2) The sample must be non-fluorescent. Even traces of fluorescent contaminants can sometimes cause difficulties.

(3) The sample volume required is larger than that for infrared spectroscopy although the difference is usually not significant when modern apparatus is used.

(4) Because Raman line intensity is proportional to concentration this technique is not useful for the determination of components at low concentrations. If an analytical problem involves the determination of major components only, the lack of sensitivity to low concentrations of minor components may be an advantage.

E. J. ROSENBAUM

INSTRUMENTS, TECHNIQUES, AND APPLICATIONS

When a beam of light encounters matter it is modified by reflection, absorption, and scattering. Scattering is called *Rayleigh* scattering if the frequency of the radiation is unchanged and *Raman* scattering if the frequency is shifted. Rayleigh and Raman scattering must not be confused with the re-emission of absorbed light as resonance radiation of the same frequency or as phos-

phorescence or fluorescence radiation with lower frequency than the incident light.

In order to observe a Raman spectrum a sample is illuminated with essentially monochromatic radiation, and the light scattered at right angles is collected and passed into a spectrometer for analysis. The spectrum obtained will show the strong Rayleigh-scattered parent line of the source with frequency unaffected by scattering and a discrete set of weaker lines at lower frequencies, each shifted from the parent line by a frequency corresponding to a mode of vibration of the molecules of the sample. These shifted lines are the Stokes-lines of the Raman effect. A much weaker set of lines (the anti-Stokes lines) are observed with the same frequency shifts from the parent line in the opposite direction. If the sample is a gas each of the lines might be further resolved into its rotational fine structure.

The scattering power, and therefore the intensity of Raman lines, is approximately proportional to the fourth power of the frequency of the exciting line. Hence it is advantageous to use the shortest wavelength possible, and some work has been done using ultraviolet exciting lines. However, because of difficulties with fluorescence and photochemical reactions the parent line is usually chosen to be in the visible region of the electromagnetic spectrum. The Toronto type lamps developed at the University of Toronto by Welsh and Crawford are the most popular sources. These are low pressure mercury arcs producing intense mercury emission lines and but little background radiation. They are formed as cylinders and mounted parallel to the sample tube or as helixes spiraling about the tube. In order to increase the efficiency of the sources, they are usually mounted in an enclosure coated with a material of high diffuse reflectance such as magnesium oxide. The light from the source is passed through a filter before being allowed to enter the sample tube. This serves to eliminate unwanted lines from

the source, background radiation, fluorescence, photochemical reactions, and overlapping Raman spectra originating from different exciting lines. A commonly used filter for use with the 4358A mercury line consists of a water solution of sodium nitrite and praseodymium nitrate in a transparent tube surrounding the sample tube.

Originally, Raman spectra were taken photographically on sensitive spectrographic plates. The integrating action of the film permitted observation of the very feeble Raman lines, and exposures of several days were not uncommon. Photographic recording is still used to some extent, but photomultiplier tubes and electronic recorders have dominated for several years. Formerly the photomultipliers were refrigerated to subdue noise, but recent improvements have made this unnecessary although detectors must still be specially selected for low noise. The radiation reaching the phototube is usually chopped in order to take advantage of

the stability and high gain attainable with AC amplifiers.

Raman spectra are exceedingly weak and this requires that spectrometers of high light gathering power be used. Aperture ratios of $f/4.5$ are common and some instruments have been constructed with apertures as large as $f/0.7$. The ratio of slit height to focal length is important in defining the "speed" of spectrometers using photoelectric detectors. The Cary instrument (Figure 1) uses two parallel slits each 10 cm in height, illuminated through an ingenious image slicer which converts the image of the sample tube cross-section to a long slit-filling rectangle.

The resolving power necessary for satisfactory Raman spectroscopy is rather large. Consider that an infrared spectrometer with a resolving power of 1000 will separate two lines 1 cm^{-1} apart at 1000 cm^{-1} , whereas similar resolution in the Raman spectrum requires a resolving power of 20,000 when

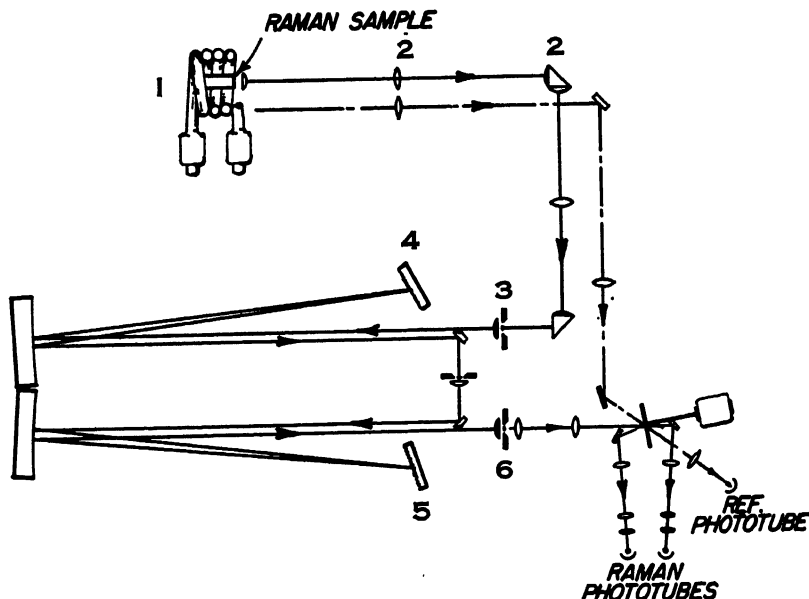


Fig. 1. Optical path of Cary Raman spectrophotometer. Light from the source (1) is scattered by the sample, shaped by the image slicer elements (2) to fill the parallel entrance slits (3), dispersed into a spectrum by two gratings (4 and 5), passed through the exit slits (6), and detected by the phototubes. Source intensity is monitored by the reference phototube. (Courtesy of Applied Physics Corporation)

RAMAN SPECTROSCOPY

using 5000Å exciting radiation. Consequently, large dispersing elements and multiple prism and grating arrangements are used in the construction of Raman spectrographs. A further requirement for spectrographs used with photographic detectors is high linear dispersion because of the graininess of high speed emulsions.

Samples to be studied by Raman spectroscopy are confined in sample tubes of glass or quartz. One end of the tube is closed by a window through which the scattered light passes. The other end is usually blackened to reduce stray light. The scattering tube is mounted concentrically in one or more additional transparent cylinders containing filter solutions and circulating thermostat liquids.

The easiest samples to handle are pure liquids or solutions. Until recently, 10 to 50 milliliters of sample were required, but capillary tubes having volumes as small as 0.05 milliliter can now be used with modern instruments. It is necessary to free samples from sources of undesirable scattering such as dust or turbidity and from colored or fluorescent materials. Treatment by percolation through adsorbents and distillation directly into the sample tube is beneficial. Stubborn cases of fluorescence or color require special approaches such as efficient optical filtering of the troublesome radiation, addition of fluorescence-quenching materials to the sample, or use of different exciting lines. Raman spectroscopy has actually been carried out with exciting lines in the photographic infrared to avoid these difficulties.

Gas samples are studied by means of Raman spectroscopy, but the diffuse nature of gases requires the use of large sampling tubes if weak lines are to be observed, complicating the design of the irradiation system. High pressure tubes have been used to concentrate gaseous samples, but rotational structure is broadened and lost. Multiple pass scattering tubes have been devised to

intensify spectra by effectively using the same volume of sample several times.

Solid samples are also studied in Raman spectroscopy, but the difficulties due to excessive general scattering are severe in the case of polycrystalline materials. This is sometimes reduced by immersion of the crystallites in a transparent liquid of the same refractive index and by filtering the parent line from the scattered light before it arrives at the spectrometer slit.

A significant property of Raman lines is their state of depolarization. A number of techniques have been devised for measuring the depolarization ratio. A widely used method requires two spectra, one recorded with the incident light polarized perpendicular and one with the light polarized parallel to the direction in which the scattered light is observed. The ratio of intensities of a line in the two spectra is its depolarization ratio, $\rho = I_{\perp}/I_{\parallel}$. A line is said to be depolarized if ρ has the value $\frac{1}{2}$, and polarized if ρ is less than $\frac{1}{2}$. Polarizers constructed of sheets of "Polaroid" are convenient for wavelengths between 4200 and 6000Å. Polarization measurements are complicated by such factors as the polarizing properties of optical elements of the spectrograph and the convergence of the radiation beam.

The applications to which Raman spectroscopy can be put are very nearly the same as infrared spectroscopy because both types of measurement deal with molecular vibrational transitions. However, because of fundamental differences in the two effects they often provide complementary information, with one type of measurement yielding data not supplied by the other.

Perhaps the most common application of molecular spectroscopy is the identification of an unknown compound by comparison of its spectrum with spectra of known substances. Raman spectroscopy is useful in this work, just as is infrared spectroscopy, because of the "finger-print" property of vibrational spectra. Each molecule has its own

unique spectrum, although the differences can be quite subtle for similar compounds. A vast number of Raman spectra have been recorded and Raman data are to be found scattered throughout the literature and occasionally collected in books and articles.

Raman spectroscopy can be used for quantitative analysis with about the same degree of success as infrared, and with the same limitations due to interferences by band overlap. Multi-component analysis is performed by measuring the lines of the pure constituents separately and developing a set of equations to be used in analyzing mixtures. Raman analysis of colorless solutions shares with emission spectroscopy an advantage over absorption spectroscopy, viz., signals are directly proportional to concentrations. Raman analysis of colored solutions is more complicated but nonetheless quite feasible.

Often a complete identification of a specimen is not possible, or even necessary, but a functional group characterization is desired. Nature has provided that certain atomic groupings in molecules vibrate more or less independently of the rest of the molecule. This permits the detection of certain functional groups by studying Raman or infrared vibrational spectra, provided that the vibration in question produces a signal of detectable magnitude. Because of the differences in relative intensities encountered in the two effects some functional groups are more readily determined by means of Raman spectroscopy and others by infrared. For example, the stretching vibration of the —C—S— link occurs with a frequency near 650 cm^{-1} . This transition is so weak in the infrared absorption spectra of sulfides as to be nearly useless for determining the presence of the group, but the Raman line is quite intense.

A complete knowledge of the vibrational spectrum of a substance is useful in elucidating the structure of its molecules and is essential for the calculation of its thermodynamic properties. Because of selection rules

some species of vibrational transitions cannot be observed in the Raman effect while others are forbidden to appear in infrared absorption spectra. In the case of a molecule having a center of symmetry an exclusion principle operates and a vibration cannot be active in both effects. Hence both infrared and Raman spectra must be obtained for a complete determination of the vibrational transitions of a molecule. Further clues to the nature of molecular vibrations are found in the depolarization ratios and contours of Raman lines. Only totally symmetric vibrations can produce polarized lines and these tend to be relatively sharp and strong, while lines from non-totally symmetric vibrations are depolarized and usually broad. In a few cases the rotational fine-structure of Raman lines of gases have been resolved and analyzed providing a means of determining the moments of inertia and interatomic distances.

REFERENCES

1. DUDENBOSTEL, B. F., JR., "Raman Spectroscopy: Instrumentation and Application", *Molecular Spectroscopy*, Institute of Petroleum, London, 1954, pp. 20-26.
2. HIBBEN, J. H., "The Raman Effect and its Chemical Applications", New York, Reinhold Publishing Corp., 1939.
3. KOHLRAUSCH, K. W. F., "Der Smekal-Raman Effect", J. Springer, Berlin, 1931; *Erganzungsband 1931-1937*, J. Springer, Berlin, 1938.
4. MIZUSHIMA, SAN-ICHIRO, "Raman Effect" *Handbuch der Physik*, S. Flugge, ed. Band XXVI, Licht und Materie II, pp. 171-243.
5. HIBBEN, J. H., "Raman Spectra", *Physical Methods in Chemical Analysis*, Vol. I, W. G. Berl, ed., Academic Press, New York, 1950, pp. 405-423.
6. GLOCKLER, G., "The Raman Effect", *Rev. Mod. Phys.*, 15, 111 (1943).
7. STOICHEFF, B. P., "High Resolution Raman Spectroscopy," *Advances in Spectroscopy*, Vol. I, H. W. THOMPSON, ed., Interscience Publishers, New York, 1959, pp. 91-174.

JAMES E. STEWART

THEORY*

Raman spectroscopy, since its beginning in 1928, has been of great use in the elucidation of the structures of molecules, in the study of the interactions between molecules, in the spectrochemical analysis of unknown mixtures, and in the provision of data for the calculation of thermodynamic properties. Sir C. V. Raman (an Indian physicist) himself would no doubt have been astounded if he could have foreseen the wide range of applications of the effect which now bears his name and for the discovery of which he received the Nobel Prize. Thousands of articles have appeared on this subject and it is still an active field of investigation.

A Raman spectrum consists of a group of lines that appear on a photographic plate after the light scattered from molecules has been passed through a dispersing prism and brought to a focus on the plate. The Raman effect is a light-scattering phenomenon, not a matter of absorption or emission of light by the molecules.

Suppose, for example, that blue light of wavelength $4359.6 \text{ \AA}$ is passed vertically upward through a tube containing CCl_4 . The light scattered horizontally by the CCl_4 molecules is found to consist primarily of light of the same wavelength (Tyndall effect) and this produces a greatly over-exposed line (Rayleigh line) on the photographic plate. But the scattered beam also contains weaker light of wavelengths greater than $4359.6 \text{ \AA}$ (Stokes lines) and still weaker light of wavelengths less than $4359.6 \text{ \AA}$ (anti-Stokes lines). The appearance of this light of changed wavelength is known as the Raman effect and the corresponding lines constitute the Raman spectrum of CCl_4 .

It is customary to list not the wavelength of the Raman line, but rather the reciprocal of the wavelength, called the *wave number* σ (number of waves per cm). Or, since this is

a large number, to list simply the difference $\Delta\sigma$ in the wave number of the Raman line and that of the incident light. The $\Delta\sigma$ values are known as the *Raman displacements*. If the relative intensity of the Raman line is designated by I , the $\Delta\sigma(I)$ values for the principal lines in the Raman spectrum of CCl_4 are 217(7), 314(9), 459(10), 762(4), and 790(4) K (K = kayser = wave/cm).

For other molecules, different displacements and relative intensities are obtained. Thus for CCl_3H , the principal $\Delta\sigma(I)$ values are 262(10), 366(7), 667(8), 762(6), 1216(2), and 3018(3) K; for CCl_3D , they are 262(10), 366(9), 650(7), 737(1), 908(1), and 2255(2) K; and for CH_3I , they are 523(10), 892(0), 1241(2), 1430(0), 2948(3), and 3048(1) K. No two compounds have the same Raman spectrum.

Another characteristic of the Raman line is the polarization state of the light that produced it. By placing a suitable polarizing device in the path of the scattered light, each Raman line can be divided into a strong part and a weak part. The intensity of the strong part I_s corresponds to the horizontal component of the electric vector in the scattered beam, that of the weak part I_w to the vertical component. The ratio $I_w/I_s = \rho$ is called the depolarization factor of the Raman line. If $\rho = \frac{1}{3} = 0.33$, the line is depolarized; if less than this, it is polarized. The $\Delta\sigma(I)\rho$ values of CCl_4 , for example, are 217(7)0.85, 314(9)0.87, 459(10)0.07, 762(4)0.84, and 790(4)0.83 K. The first two lines are thus depolarized, the third strongly polarized, and the last two lines slightly polarized. Each compound is characterized by the $\Delta\sigma(I)\rho$ values of its Raman spectrum.

The existence of a scattered radiation depends upon the fact that the incident light wave induces a dipole moment in the molecule. This induced dipole moment varies periodically with certain frequencies, and hence light of these frequencies is sent out by the molecules in all directions.

The change in wavelength that occurs dur-

* From "The Encyclopedia of Chemistry", Supplement, 1958, p. 244.

ing the scattering process can be related to the change in the energy of the molecule when the incident photon is scattered. The energy of the photon is $hc\sigma_i$, where h is Planck's constant, c is the velocity of light in a vacuum, and σ_i is the wave number of the incident radiation. The Raman effect thus results from a transfer of energy from the photon to the molecule, or vice versa.

A considerable amount of information about a molecule can be deduced from the Raman spectrum. From the pure rotational Raman spectrum of a diatomic molecule, for example, one can obtain the effective moment of inertia in the lowest vibrational energy state and from this the effective internuclear distance for this state. The moments of inertia obtained in this way for HCl and N₂ are, respectively, 1.649 and 8.342 amu Å² and the corresponding internuclear distances are 1.297 and 1.097 Å.

Homonuclear molecules like H₂ and N₂ yield no pure rotational infrared spectrum because they have no permanent dipole moment and therefore can be studied only by the Raman effect. In their case the pure rotational spectrum yields—in addition to the effective moment of inertia and effective internuclear distance for the lowest vibrational state—the symmetry of the eigenfunction with respect to an interchange of nuclear coordinates, the nuclear spin, and the form of statistics (Fermi-Dirac or Einstein-Bose) that must be used in statistical calculations.

From an analysis of the vibrational-rotational bands, one can obtain the classical vibrational frequency of the diatomic molecule, the moments of inertia and internuclear distances for higher vibrational states, the force constant, the dissociation energies, the zero-point energy, the potential energy curve as a function of the internuclear distance, and the rotational and vibrational energies needed for thermodynamical calculations.

Polyatomic molecules are more complex and therefore cannot be treated as rigorously

as diatomic molecules. Nevertheless, one can still obtain for the simpler molecules the moments of inertia, internuclear distances, and interbond angles. For larger molecules, as well as the smaller ones, one can obtain the constants in the potential energy expression (force constants) and the vibrational frequencies needed for the calculation of the thermodynamic properties.

Frequently it is possible to determine the structure of a polyatomic molecule from the spectral data. For, when the molecule has certain elements of symmetry (rotational axes, symmetry planes, etc.), there are selection rules which tell how many polarized and depolarized Raman lines should appear in the spectrum for each of several possible structures. By comparing these predictions with the experimental results, one can obtain an indication of the correct structure.

The Raman spectral data also are useful in detecting interactions between molecules. Thus, for example, when hydrogen bonding is present the Raman displacements corresponding to the C—H and C=O vibrations appear at values distinctly lower than their normal values. Also, one can study the coordination complexes of silver ion with unsaturated hydrocarbons. In such complexes, the $\Delta\sigma$ values corresponding to the C=C and C≡C bonds are lowered by about 65 and 100 K, respectively, from the normal values.

The $\Delta\sigma$ values corresponding to the vibrational frequencies of certain groups within the molecule often change little from one molecule to another. The appearance of these values in the Raman spectrum is thus evidence for the existence of these groups. Thus there is a $\Delta\sigma$ value near 3300 K for —C≡C—H, 3000 for C—H (non-acetylenic), 2250 for C—D (non-acetylenic), 2118 for monosubstituted acetylenes R—C≡C—H, 2233 and 2300 for disubstituted acetylenes R—C≡C—R, 1700 for C=O, 1600 for C=C, 700 for C—Cl, 500 for C—Br, etc.

Monosubstituted benzenes C₆H₅R are characterized by a group of lines having

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$\Delta\sigma(I)_\rho$ values near 618(5)0.8, 1001(10)-0.1, 1029(7)0.3, 1156(4)0.8, 1176(4)0.8, 1588(6)0.7, and 3058(9)0.3. The $-\text{CH}_3$ group has $\Delta\sigma(I)_\rho$ values near 1378(4)0.6, 1441(1)0.9, 2921(10)0.1, and 3070(2)0.9. The $-\text{CH}_2-$ group has $\Delta\sigma(I)_\rho$ values near 1412(1)0.8, 2985(10)0.1, and 3050(2)0.9. Substituted ethylenes are characterized by a group of lines between 1200 and 3100 K whose $\Delta\sigma(I)_\rho$ values depend upon the position and the extent of the substitution and upon the presence or absence of conjugated bonds.

Quantitative analysis also can be done by use of Raman spectral data since the intensity of a Raman line of a compound is proportional to the concentration of this compound in a mixture. This may be accomplished either by a comparison of the intensity of the line with that of an internal standard, such as the 459 K line of CCl_4 when 2 cc of this compound is added to 25 cc of the sample, or by a calibration for each system based upon a few mixtures of known composition made from compounds of high purity.

The precision of the analysis with the calibration method and with photographic recording is indicated by the following results of Rosenbaum, Martin, and Lauer. In an analysis of a mixture containing *p*-ethyltoluene, pseudocumene, *m*-ethyltoluene, and mesitylene, the average deviation of their results from the known composition was 0.75%; for a mixture containing *o*-xylene, *m*-xylene, *p*-xylene, and ethylbenzene, the average deviation was 1%; for a mixture

containing *p*-ethyltoluene, *m*-ethyltoluene, *o*-ethyltoluene, mesitylene, and pseudocumene, the average deviation was 1%; and for a mixture of 2,2,4-trimethylpentane, 2,3,4-trimethylpentane, and 2,3,3-trimethylpentane, the average deviation was 1.3%.

Using photoelectric recording and a modified internal standard method in which the CCl_4 was contained in an identical Raman tube instead of being added to the sample itself, Rank and Wiegand made numerous analyses of aromatic hydrocarbon mixtures containing from 2 to 8 components and showed that an accuracy of about 2% was obtainable for the major components.

After the fundamental vibrational frequencies of the molecule have been determined from the Raman (and for certain symmetrical structures also from the infrared) spectral data, the heat content, free energy, entropy, and heat capacity for the ideal gaseous state can be calculated for various temperatures, provided the internuclear distances and interbond angles are known from rotational spectra, electron diffraction, or microwave spectra. The translational and rotational contributions are calculated from well-known formulas and added to the vibrational contributions obtained from tables which list the values of the thermodynamic functions for various values of $\Delta\sigma/T$ (T = temperature in $^\circ\text{K}$). The values thus calculated are usually more reliable and extensive than the observed values.

FORREST F. CLEVELAND

SOLAR SPECTROSCOPY

Solar spectroscopy is the oldest of the divisions of spectroscopic science. The history of the efforts extended by its practitioners toward the attainment of perfection

in observation and interpretation is partitioned by several periods when within a few years' time, crucial experimental results were obtained. Newton's experiments (1672) serve

to separate the early and rather haphazard observations of ancient days from the controlled experimentation that is a characteristic of modern investigations. For this reason, Newton's studies of the sun's spectrum are often taken as the beginnings of solar spectroscopy.

More than 100 years later (1817), a second era of rapid development was initiated by Fraunhofer, who not only produced a very useful map of the solar spectrum, but, more importantly, invented spectroscopic apparatus used today in all powerful instruments. Although Fraunhofer was aware of the existence of a bright yellow line in the spectra of flames, and realized the importance of the coincidence of this yellow line with the dark line that he had labeled "D" in the solar spectrum, he did not permit himself to be diverted from the task of perfecting astronomical telescopes by this promising new field of research.

In the 1840's an important principle of modern astronomical spectroscopic analysis was first published by Doppler (1842), and later (1848) more correctly stated by Fizeau. Doppler's principle asserts that the observed color of the light emitted by a body may be changed as the relative motion of the observer and the emitter changes. Fizeau's version of the principle states that the observed wavelength of a given spectral line emitted from a moving body will differ from the wavelength of the same line, emitted from a body at rest, by an amount equal to the product: the wavelength at rest times the ratio of the line of sight velocity of the source and the observer to the velocity of light. In this form, the principle has immediate application to the spectroscopic measurement of astronomical velocities, and it is fundamental not only to the determination of the motions of various parts of the sun, but also to the derivation of temperatures based on the random velocities of the atoms in the solar atmosphere.

About ten years after the introduction of Doppler's principle, Kirchhoff (1859) again directed attention to the enormous significance of the coincidences between the absorption lines in the sun and the bright lines in laboratory sources. Kirchhoff was able to deduce a number of important laws of spectrochemical analysis from the data that had accumulated since 1817. Solar astronomers rapidly applied the generalizations of Fraunhofer, Doppler, Fizeau, and Kirchhoff to a series of spectroscopic comparisons of the sun and laboratory sources during the last third of the 19th century. These researches established the bases for the study of the temperatures and pressures in the solar atmosphere, and resulted in a remarkably complete identification of the chemical elements present. Indeed, they led to the discovery of helium, then unknown on earth, in 1868.

Near the beginning of the 1900's Rowland published a table of solar spectrum wavelengths that summarized much of the earlier work and presented a large amount of new data. Rowland's table is composed of wavelengths for the solar lines derived from new measurements, identification of chemical elements, based on coincidences of the absorption lines in the sun with emission lines from laboratory sources, and estimations of line strengths. The new results of the table were the first to be based entirely on spectrum photographs. They were also the first fruits of the use of a concave diffraction grating, an instrument invented and developed to near-perfection by Rowland. The publication of Rowland's table (which is still being revised and brought up to date) may be said to mark the start of modern solar spectroscopy.

Some Forms of Solar Spectroscopes. All the early results were obtained, necessarily, with rudimentary apparatus which has evolved through the application of technical advances into what is now a more or less definite type of instrument. It is this particular instrument type that distinguishes

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solar spectroscopy from the other branches of the science.

Thanks chiefly to Rowland's revolutionary achievements, the modern solar spectroscope is constructed around a nearly perfect diffraction grating. Rowland's investigation of the sun's spectrum made use of concave diffraction gratings of his own manufacture in the distinctive arrangement illustrated in Figure 1. The distinguishing features of the Rowland mounting are: (1) the slit and focal surface lie on a circle (the Rowland Circle) the diameter of which is equal to the radius of curvature of the grating surface; (2) the angle defined by the lines joining the three points: the center of the grating, the center of the slit, and the center of the spectral image, is a right angle. The first of these characteristics is common to a large number of concave grating spectroscopes, viz.: the Paschen-Runge, the Abney, the radius, and the Eagle mountings. These modifications of Rowland's original mounting have been used only occasionally for solar spectroscopy, but the grazing-incidence modification of the Paschen-Runge mounting (indicated by S_2 = entrance slit, and $COSI_2$ = center of spectral image

in Figure 1) will probably be much used in primitive investigations of the sun's ultra-violet spectrum from satellites and rockets.

Perhaps, among the types of spectroscopes that employ concave gratings as their means of dispersion, the most important are those which, in addition to the grating, use a lens, or mirror, to irradiate the grating with a collimated beam. Three examples are shown in Figure 2, a, b, and c. Figure 2a is a sketch of an application of the concave grating to the photography of the thin crescent of the sun that is formed just before, and just after, the total phase of a solar eclipse (the flash spectrum). The concave grating alone forms an efficient spectroscope, for the extremely fine crescent between the edges of the sun and moon simulates a slit source at a practically infinite distance, and very excellent spectra may be obtained with this simple arrangement. The Wadsworth mounting, shown in Figures 2b and c, is used mainly in special investigations which require the recording of radiation throughout a continuous, and wide, range of wavelengths, and in which high dispersion may be sacrificed.

In the recent past, instruments employing

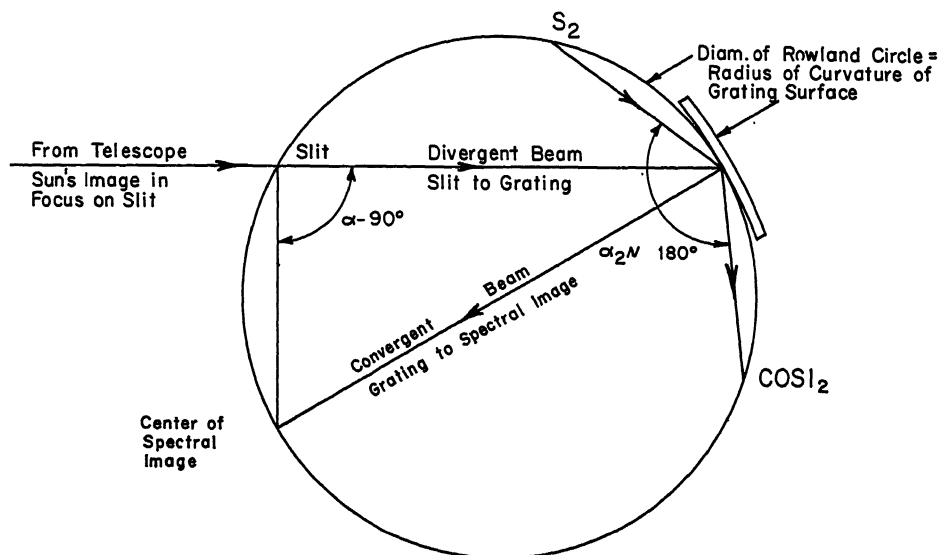


FIG. 1. Rowland mounting of a concave grating.

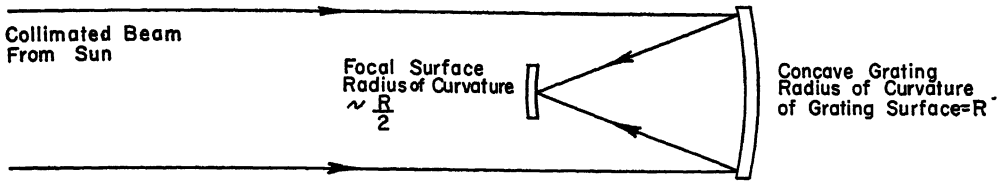


FIG. 2a. Concave grating in flash spectroscope.

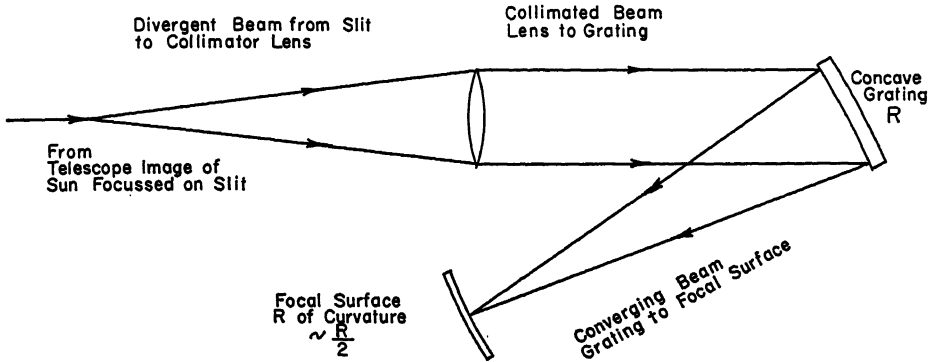


FIG. 2b. Wadsworth mounting of a concave grating with lens as collimator.

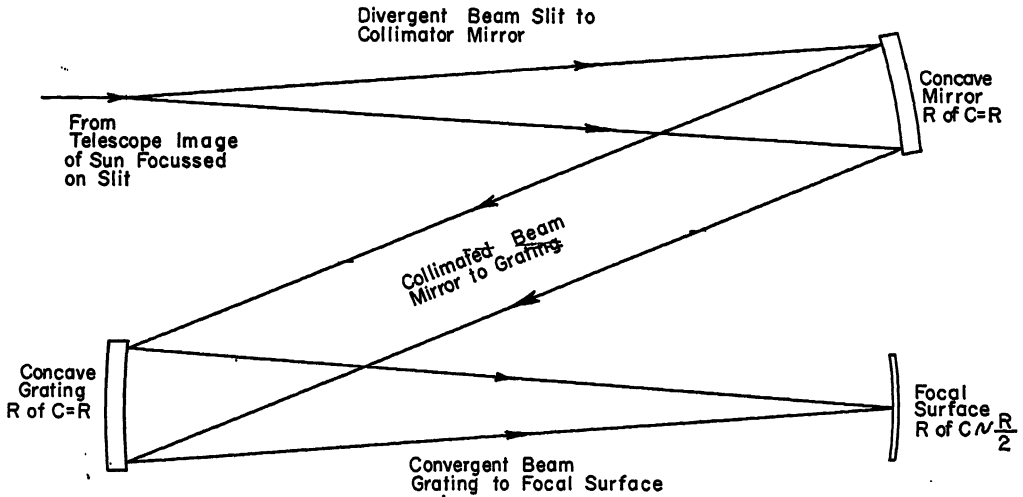


FIG. 2c. Wadsworth mounting of a concave grating with mirror as collimator.

plane gratings in an autocollimating arrangement, shown in Figure 3, have dominated solar research. The essentials of these instruments are: (1) a plane diffraction grating, as nearly perfect as possible, and with as large a ruled surface as can be produced; (2) a collimator-camera lens as nearly perfect as possible, and with a focal length of the order

of 30 meters. At the present (1959) stage of technical progress, gratings of the best quality may have ruled surfaces of the order of 200×250 millimeters. The aperture of the lens is chosen to provide full illumination for the grating. Two important advantages of this mounting are: the ease with which spectra of different orders may be studied, since

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the rotation of the grating about the central groove will direct any possible spectral order or wavelength to the focal plane; and the relatively small space required for housing the instrument. The space requirement is important because it is often necessary to control the temperature within the spectrograph very closely, or even to evacuate the instrument, in order to obtain the best spectroscopic definition.

A plane diffraction grating is often used at eclipse times for the observation of the flash spectrum in an arrangement shown schematically in Figure 4. This use of the plane grating is analogous to the use of the concave grating (Figure 2a) for the photography of the flash spectrum. Spectra obtained with these simple spectroscopes permit a derivation of the distribution of the various chemical elements at different heights in the sun's outer layers.

Many of the most recently constructed spectroscopes for purely solar research emphasize optical systems that are composed entirely of reflecting surfaces. In a common form (Figure 5), a concave mirror is used as a collimator to direct a collimated beam of radiation to a plane diffraction grating. The diffracted beam from the grating is received by a second concave mirror which, in turn, forms an image of the spectrum. In this arrangement the slit, grating and focal plane can be arranged close together near one end of the instrument with the collimator and camera mirrors at the other end. Many of the advantages of the autocollimating plane grating instrument are retained in this all-reflecting construction.

A rather similar scheme (Figure 6), known as the Ebert spectroscope, has found application to those studies of the sun that require the photography of long arcs along the

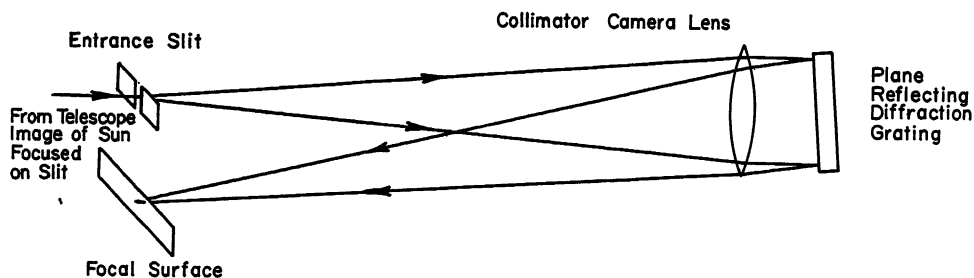


FIG. 3. Autocollimating plane-grating spectroscope.

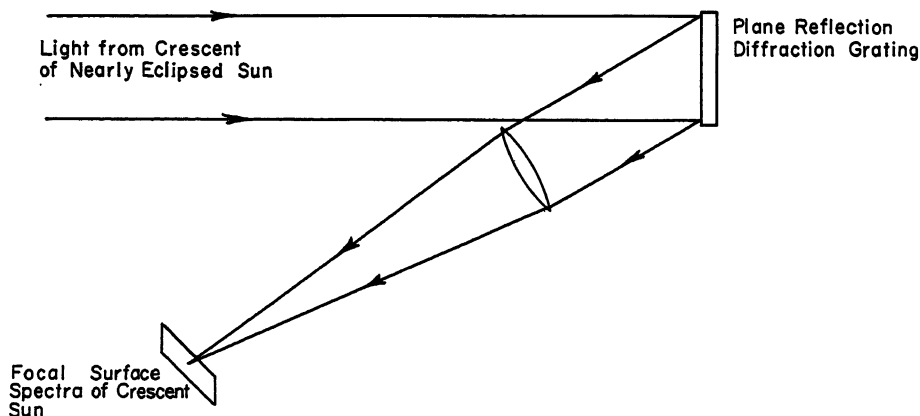


FIG. 4

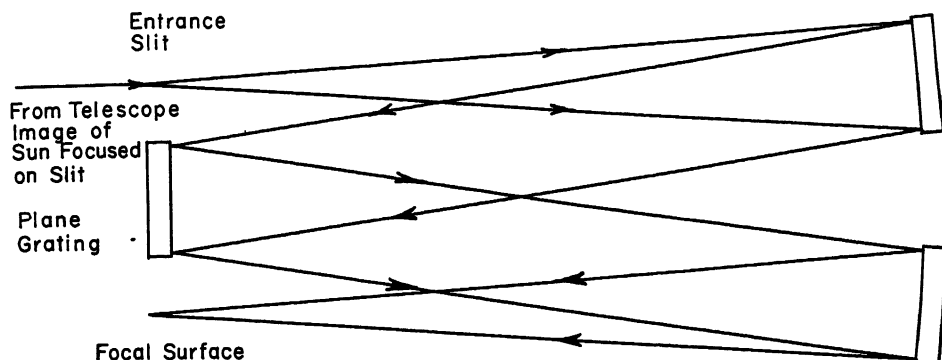


FIG. 5

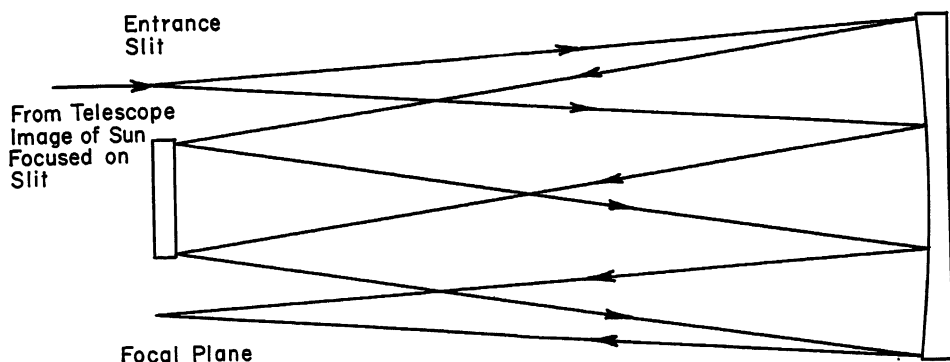


FIG. 6

solar limb, and also to investigations demanding the transmission of maximum power to a detector.

The descriptions just given cover the principal forms of spectroscopes used in solar astronomy. Frequently, spectroscopic instruments, including interference filters and interferometers, are combined into complex instruments suitable for specialized investigations that require the maximum spectroscopic refinement.

The Interpretation of Solar Spectroscopic Observations. Interpretations of the observations obtained with powerful spectroscopes have led to a high degree of perfection in the descriptive spectroscopy of the solar spectrum. As indicated above, the first detailed description, supported by measurements, was published by Fraunhofer in 1814. A map of the solar spectrum, published by

Angstrom in 1868, constituted a considerable advance over the earlier work and provided spectroscopists with their first useful standards of wavelengths. The publication of Rowland's description of the solar spectrum in his "Preliminary Table of Solar Spectrum Wavelengths" began in 1895. It included wavelengths, intensity estimates, and identifications of the probable chemical sources of many of the solar lines. It achieved such high standards that it set a pattern for the final efforts in this field. In 1928 the Mount Wilson Observatory published a very considerable extension and refinement of Rowland's preliminary work. A further additional refinement of the listing of the wavelengths of all solar lines, their intensities and identifications, is in the process of publication by the International Astronomical Union.

One of the parts of the description of the

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solar spectrum can be correctly labeled as a qualitative spectroscopic chemical analysis of the sun's atmosphere. Such an analysis depends chiefly on knowing the positions of the lines in the spectrum and their total absorptions. In earlier works, and indeed in many of the most modern descriptions, total absorptions are eye estimations of a rather undefinable quantity, called the "intensity of the line." The "intensity of the line" is a

guess at the total amount of energy absorbed from the continuous background of the solar radiation in the region of the spectrum line (Figure 7). The most direct and widely used method of identifying solar lines with those of known atoms and molecules is by direct comparison with laboratory spectra (Figure 8). Such identifications are based on the precise coincidence in the positions of the spectral line in the solar and terrestrial

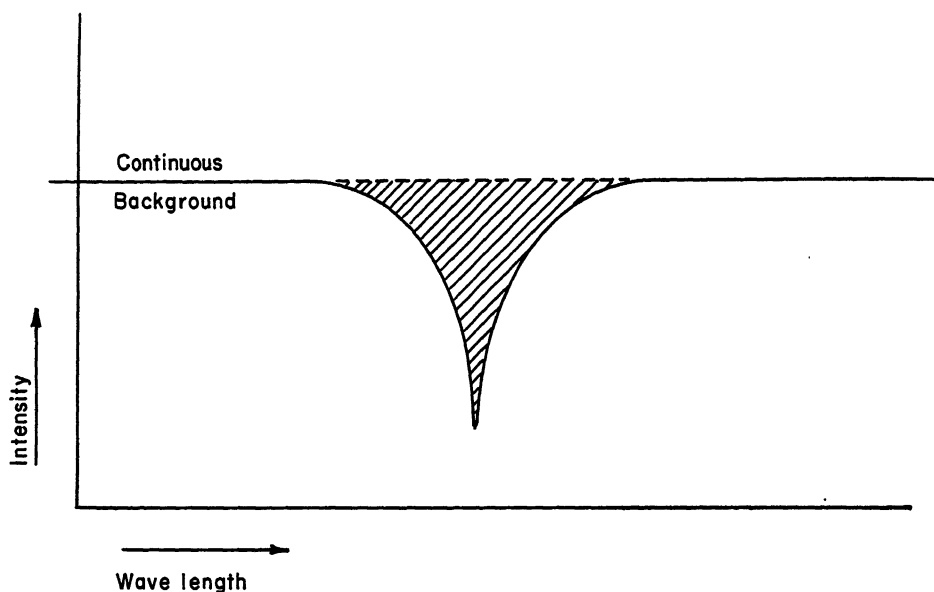
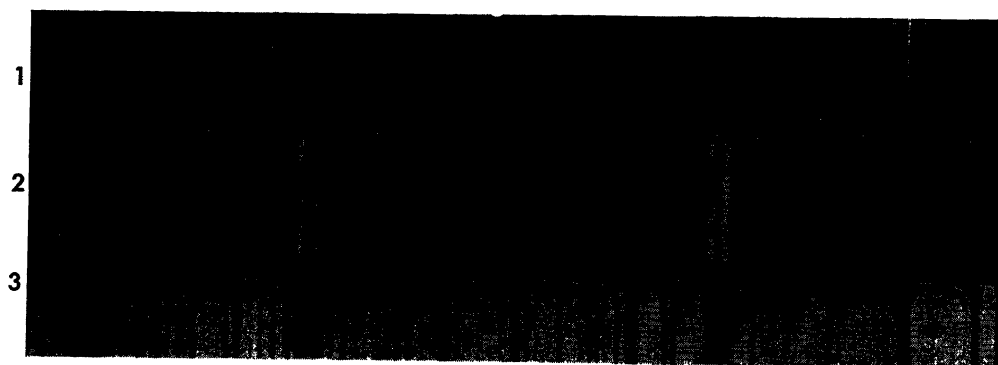


FIG. 7. "Intensity of line" is the cross-hatched area.



(Courtesy of the California Inst. of Technology Press)

1. Scale of wave lengths
2. Laboratory spectrum of iron arc
3. Spectrum of sun

FIG. 8. Comparison of spectrum of iron arc and the spectrum of the sun. Note the close coincidence in position between the laboratory lines and the sun lines, and the approximate coincidence in intensities.

spectra, and on good agreement, line by line, in the intensities, even though the solar lines appear dark in absorption and the terrestrial lines are bright in emission. Direct identifications of this kind are often supplemented by the prediction of line positions. The wavelengths of the predicted lines are calculated from differences between atomic energy levels that have been derived from laboratory spectra. The prediction method has been particularly advantageous for the identification of unusual lines. The appearance of the lines of neutral Fe is especially favored in the solar spectrum because of the appropriate temperatures and the long path length of the photosphere, hence, this spectrum is more fully represented in the sun than in any possible combination of terrestrial sources. The large number of the lines that are identified in the solar spectrum as belonging to Fe are so assigned on the basis of predicted wavelength.

A recently published compilation of the identifications that are considered reasonably certain lists about 67 chemical elements. The identifications are based on atomic spectra with the exception of those for B and F, which appear only in the spectra of molecular compounds. The terrestrial elements the presence of which cannot be established in the solar spectrum can be accounted for on the bases of low abundance, unobservable location of the sensitive lines in the spectrum, and the relative instability of some of the radioactive atomic species. In addition to the atomic lines there are some molecular band systems also identified. Fourteen diatomic molecules are certainly present and there is a possibility of nine others. Except for the bands of C_2 and CN all of the band lines are normally weak. In fact, many of them are completely absent from the normal solar spectrum and are detected only in spectra of sunspots. Except for CO, the fundamental and first overtone vibrational bands of which are observed in the infrared part of

the solar spectrum, all of the bands so far discovered originate in electronic transitions.

More than 30,000 lines have been recorded in the solar spectrum.

Once the chemical origin of the solar absorption lines has been established a possible next step is to attempt to use the spectral features for a quantitative chemical analysis. Although the qualitative chemical analysis of the solar atmosphere can be successfully established on the basis of subjective estimations of the energy absorbed by the spectrum lines, measurements are required for the quantitative analysis. However, one must point out in passing that it is true that a first, approximately correct, quantitative estimation of the abundance of the chemical elements in the solar atmosphere was based on eye estimates alone. Several detailed measurements of the energy absorbed by the spectrum lines of the given chemical element in the solar spectrum are being made in the hope that such precisely measured absorption will increase the precision of the quantitative analysis. A sample of the results of the current quantitative chemical analysis of the solar atmosphere is given in Table 1.

A complete knowledge of the chemical elements present in the solar atmosphere and of their relative abundances does not give sufficient information to make possible the prediction of the observed appearance of the solar spectrum in detail. Additional information concerning the physical state of the sun's atmosphere is required for the refinement of the theoretical prediction. The variation of the temperatures and pressures along a radius of the sun must be known. One would also like to know the extent of the magnetic and electric fields, both macroscopic and interatomic. A knowledge of the velocity field and whether it is turbulent or convective doubtless would also be helpful. Clues to the values of all of these parameters are contained in observations of the way in which the intensity within a given spectrum line varies with the wavelength within the

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TABLE 1. ABUNDANCES OF THE CHEMICAL ELEMENTS IN THE SOLAR ATMOSPHERE
(H = 12.00 by definition—12.00 is the logarithm to the base 10 of the number of H atoms.)

Atomic Number	Element	Abundance	Atomic Number	Element	Abundance
1	H	12.00	41	Nb	2.0
2	He	11.3	42	Mo	1.9
3	Li	1.0	43	Tc	Absent
4	Be	2.4	44	Ru	1.4
5	B	Appears in BH	45	Rh	0.8
6	C	8.7	46	Pd	1.2
7	N	8.0	47	Ag	0.6
8	O	9.0	48	Cd	1.5
9	F	MgF, SrF	49	In	1.2
10	Ne	Absent	50	Sn	1.5
11	Na	6.3	51	Sb	1.9
12	Mg	7.4	52	Te	Absent
13	Al	6.2	53	I	Absent
14	Si	7.5	54	Xe	Absent
15	P	5.3	55	Cs	Absent
16	S	7.3	56	Ba	2.1
17	Cl	Absent	57	La	Present
18	A	Corona	58	Ce	Present
19	K	4.7	59	Pr	Present
20	Ca	6.2	60	Nd	Present
21	Sc	2.8	61	Pm	No Data
22	Ti	4.7	62	Sm	Present
23	V	3.7	63	Eu	Present
24	Cr	5.3	64	Gd	Present
25	Mn	4.9	65	Tb	Present?
26	Fe	6.6	66	Dy	Present
27	Co	4.6	67	Ho	No Data
28	Ni	5.5	68	Er	Present?
29	Cu	5.0	69	Tm	Present
30	Zn	4.4	70	Yb	1.5
31	Ga	2.4	71	Lu	Present
32	Ge	3.3	72	Hf	Present
33	As	Absent	73	Ta	Present?
34	Se	Absent	74	W	Present
35	Br	Absent	75	Re	Absent
36	Kr	Absent	76	Os	Present
37	Rb	2.5	77	Ir	Present
38	Sr	2.6	78	Pt	Present
39	Y	2.2	79	Au	Present?
40	Zr	2.2	80	Hg	Absent
			81	Tl	Absent
			82	Pb	1.0

No elements with atomic numbers greater than 82 have been detected.

solar spectrum. The intensity wavelength function can also be determined for various positions on the solar disk. The curve representing the spectral variation of intensity within a single absorption line (Figure 7) is called the line profile, or line contour. Elaborate analyses may be based on single line profiles or on the comparison of a number of line profiles. The profiles may refer either to one chemical element or a number of lines may be chosen from among the different elements. In general, the procedure involves assumptions concerning the value of certain physical parameters and the calculation with these assumed values of a predicted appearance of the line profile under consideration. The differences between the observed and computed profiles form the bases for refinements of the assumed values. The assumptions are varied until the observed and computed profiles agree within the limits set by the errors of observation.

Great care must be exercised at all points of the design of a spectroscope for profile investigation to keep the instrumental distortions of the spectral images to a minimum. The usual forms of spectroscopes have such serious distortions that studies of line profiles have progressed very slowly.

A listing of all line profiles so far studied

would be very short indeed and the deductions of the physical conditions on the sun from observations of the changes of intensity within its spectrum remains almost completely untouched. Thus, solar spectroscopy, now that the descriptive aspects have been finished is entering the interesting phase in which the detailed physical structure of the sun will be derived.

Literature. A fundamental reference for all early work in spectroscopy is H. Kayser, *Handbuch der Spektroskopie* (Leipzig, 1900). In a number of volumes Professor Kayser has written a complete history of spectroscopic investigation.

There is no modern summary of spectroscopic investigation comparable with that of Kayser. Perhaps the best sources of information will be found scattered through the publications of the Mt. Wilson Observatory. Particularly after 1918, these publications give a running account of modern spectroscopic solar research at one of the world's leading observatories.

An excellent summary of conclusions based on solar spectroscopy will be found in Unsöld "Physik der Sternatmosphären" (Berlin, 1955).

ORREN MOHLER

VACUUM SPECTROSCOPY

With the Space Age has come a resurgence of interest in the field of vacuum or far ultraviolet spectroscopy. The vacuum of space does not denote empty space, for it is a region of intense chemical activity where far ultraviolet, x-ray and cosmic radiation—screened from the inhabitants below—triggers reactions unknown on earth. Sparse as they are, atoms of the gases combine to form ozone, nitrogen oxides and other highly reactive

compounds. The military has learned that these can destroy structural parts of aircraft, interfere with fuel combustion and play havoc with electronic devices. One way of anticipating the problems is to duplicate upper atmosphere conditions in the earth-bound laboratory. By artificially creating the radiation conditions above the earth, spectrographers hope to learn how to cope with the real problems.

To conventional spectrographers, such studies may appear deceptively simple. First, let us dispel that illusion. The vacuum ultraviolet refers to the region from about 50 to 2000Å to which air is fortunately opaque. Unlike other regions, there is no known source of "white" radiation for absorption spectroscopic measurements in this region. Black-body radiation serves the infrared; a hydrogen continuum the ordinary ultraviolet. But the only known continuum in the far ultraviolet is the Lyman source which consumes its electrodes rapidly and is too unstable for most work. The hydrogen lamp continuum becomes many-lined below 1650Å. The rare gases exhibit continua over only narrow spectral ranges. So the spectrographer doing absorption work must constantly switch from one source to another in order to cover a meaningful spectral range. From 1650–2000Å, he will use a hydrogen discharge. Between 1070–1650Å, a silent discharge using 200 mm pressure of argon may be used. Alternatively, using the same circuitry, the continuum of xenon extends from 1500 to 1900Å; krypton from 1240 to 1850Å.

But if the source is still a problem, it has its equal in the detector, photographic and photoelectric. Temperamental in other regions, photographic emulsions are even more so below 2000Å and are subject to scratching, distortion and variable sensitivity. Recently, a photoelectric detector was discovered which offers much promise. It is a sodium salicylate covered multiplier phototube. A phosphor, sodium salicylate was found to have the property of constant quantum efficiency over a wide range of the far ultraviolet. That is to say, its electrical output is identical whether it is irradiated with the same amount of energy at 2000Å or 1000Å.

While on the subject of the difficulties facing the vacuum spectrographer, it would be well to remind those of us who may be used to running dozens of samples a day, that our patience might be strained in the vacuum region. Changing samples, loading and un-

loading film—speedily done in other regions—are all time-consuming operations in far ultraviolet work.

Despite the obstacles, a good deal of practical information is currently being obtained. Take the field of reaction kinetics which may seem to be a highly theoretical subject, remote from any practical implications. Just the opposite is true, however. Consider the problem of reentry of missiles into our atmosphere. Here the nose of the missile is subjected to heat of such intensity that most solids would instantly vaporize. Part of the heat is caused when the missile catalyzes the reaction



releasing a good deal of energy. Preventing or inhibiting this reaction is thus of immediate military concern.

A unique method of studying the reaction was devised at the General Electric Missiles & Ordnance Department in Philadelphia by a group under the direction of Myerson. The first step was to dissociate molecular oxygen into atomic oxygen, the reverse of the above reaction. This may be accomplished in an RF field or through photolysis, using a flash of light around 1750Å. This wavelength is equivalent to the 8 ev required for dissociation.

Having dissociated, the oxygen atoms recombine spontaneously. To measure the recombination rate, Dr. Myerson tried three approaches: 1) studying the intensity changes with time of the molecular oxygen continuum around 1750Å; 2) measuring the intensity change of the atomic oxygen line at 1302Å; 3) through flash spectroscopy where photographs of the spectrum are taken at different delay intervals after a flash dissociates the molecule. The last technique will be discussed at greater length later.

History

Before going into further analytical potentialities of the vacuum ultraviolet, let us

ponder the region as perhaps did Schumann in the 1890's. During those pioneering days, knowledge of the region was absolutely nil. Transparent optics had to be discovered and sensitive photographic plates had to be invented if the region was to be explored. Even the prism, commonly made of quartz and the heart of all spectrographs at that time, was found to block out radiation beyond 2000Å in the ultraviolet.

Schumann's first task then was to find a suitable material for the prism. Years of systematic hunting through every natural mineral he could obtain, finally led him to calcium fluoride (fluorite) and, attesting to his thoroughness, this is still used today down to 1200Å, its cut-off point. But finding a prism material was only the first step. What the optics now transmitted, the photographic plate did not detect and the air in the spectrograph filtered out. The realization that these were three separate and distinct problems was, in itself, a tremendous achievement. We can imagine that when Schumann first discovered fluorite, he measured his success in terms of a tiny improvement in the spectrograms. Not until all three problems were solved, however, did he achieve spectrograms which really extended scientific knowledge appreciably. This collective achievement—this lifetime of work—is what has made Victor Schumann the most important contributor to vacuum spectroscopy.

After discovering fluorite, Schumann turned his efforts to the photographic plate—the second problem. The plate which he invented—if you can call the long series of trial-and-error experiments he conducted “invention”—is, like fluorite, still used today. The method of preparation which evolved is like an exotic food recipe, each step of which must be followed diligently if results are to be achieved. The plate must be stripped of most of its gelatin, heated gingerly, washed, dried and stored under just the right conditions. Even then, the emulsion produced is unstable, irreproducible and

easily scratched. It has been, nevertheless, the basic photographic plate used in this region to the present time. Workers since Schumann have shown that it is sensitive to at least 50Å.

His third, and perhaps most difficult problem, was absorption of radiation by the very air in the spectrograph. Vital to his success were a home-made vacuum pump and measuring equipment plus the ingenious gadgetry which he developed for changing wavelength and racking the camera while maintaining a vacuum. Were he not so ingenious, it is doubtful whether he would have had time—let alone patience—for his achievements. To appreciate this, we must picture not a modern, plug-in vacuum pump but a heavy, steam-operated machine with leaky valves constantly threatening to squirt oil of relatively high volatility into the spectrograph. We must think of his fragile mercury manometers rather than a neat electronic package containing a handy ionization and thermocouple gauge combination. We must remember that Apiezon wax, silicone oils, stainless steel, Pyrex glass, fused silica, Teflon, neoprene o-rings and Kovar glass-to-metal seals were undreamed of miracles. Even sealing a system vacuum tight was a major undertaking in those days when the Tesla coil (not to mention mass spectrometer) leak detector was unknown.

To accomplish his extraordinary feats without these tools and materials, Schumann had to make a painful choice in life: to devote full time to research or his business. Fortunately for science, he chose the former, sacrificing his income altogether. From age 40, his decision made, he was to devote the rest of his active life to vacuum spectroscopy, directed and financed completely by himself.

Another contributor who should be singled out for his work in the far ultraviolet is Theodore Lyman. In 1906, Lyman first used a concave grating in place of the fluorite prism and so was able to make accurate

wavelength measurements for the first time. Prior to that time, having no way of measuring the dispersion of fluorite, Schumann could only approximate wavelengths in this region. Lyman also extended the studies to 500A and developed a source bearing his name.

Using grazing incidence illumination of the grating, Compton and Doan (1925) were able to study soft x-rays, above 10A. They discovered that most materials have superior reflectivity below 500A using grazing rather than normal incidence. The discovery, an unexpected one, was not made until about 19 years from Lyman's first work with gratings, but, within two years, Hoag used a similar grazing-incidence mounting for the vacuum ultraviolet and celebrated the "holing through" to the x-ray region.

A hot spark (sometimes referred to as a vacuum spark), originally discovered by Wood and rediscovered by Millikan in 1921, is significant historically. It was this source that permitted the merger of the x-ray and ultraviolet. In fact, the hot spark emits x-rays of such intensity that care must be taken in using it. The source has fallen into disuse, however, both because of its danger and because it is very unstable, eating away its electrodes at a rapid rate. The eroded particles of the electrodes, tungsten or other refractory metals, sputter against the slit jaws or even the grating with such violence that they cause damage.

To shorten this historical account, permit a jump to the present. During the past thirty years, the spectra of most of the elements have been accurately charted, photographic and vacuum techniques vastly improved, lithium fluoride has been found to transmit further into the vacuum region than fluorite, the multiplier phototube was invented which, with its attendant electronic amplifying and recording systems, is a tremendous improvement over the delicate photographic plate.

An Analytical Tool

A paper by Jones and Taylor, published in 1955¹ is about the most complete account of the absorption applications of far ultraviolet radiation as a tool in analytical chemistry. Among other things, these chemists found that, in this region, the spectra of unsaturated hydrocarbons consist of broad, almost structureless bands. The spectra of members of a particular series were found to be so similar that this region may be used to determine the total concentration of this hydrocarbon series. On this basis, the authors indicate the possibilities of running a total olefin determination. Vacuum ultraviolet analysis thus offers a tool to complement more specific measurements on saturated hydrocarbons in the ultraviolet, visible and infrared. On the other hand, Jones and Taylor found that, with such substances as conjugated diolefins, individual members of the series did give rise to characteristic spectra which could be used for specific identification. Fig. 1 shows typical results.

In emission, comparatively little has, as yet, been done in the vacuum region. Spectra of many elements have been studied and reported in the region below 2000A, but the region has been put to little practical use. This, despite the fact that several elements have their strongest lines here. Very likely, the answer to this little riddle lies in the very nature of progress. Twenty years ago, the spectrographer was content with buying a basic spectrograph and setting up his own auxiliary equipment. Now, he is used to buying a complete instrument in which the sample goes in one end and the answer comes out the other. Vacuum spectroscopy has a long way to go to reach this landmark.

Let us question once more the significance of the vacuum ultraviolet, especially from the standpoint of why certain data must be obtained here and cannot be obtained in other spectral regions. Expressed in electron volts, the excitation potential of an atom is defined as the energy required to elevate an

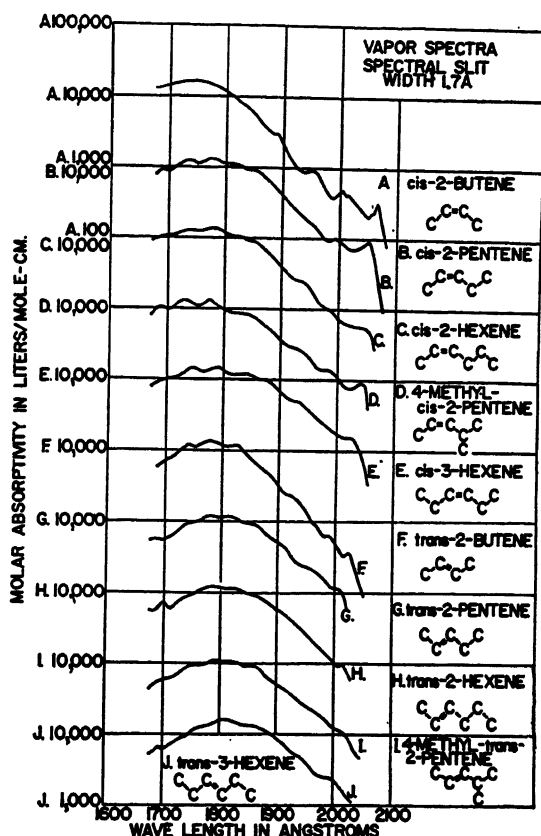


FIG. 1. Far ultraviolet spectra of vapors of C_4 to C_6 1,2-dialkyl ethylenes.¹

electron from one orbital level to another. Quantum mechanics has shown that 1 to 100 ev corresponds to the region from 12,500 to 125A—the near infrared to the far ultraviolet. The excitation potential of many atoms lies above 6.3 ev or below 2000A. Thus the most sensitive lines of many of the non-metals, the metalloids, the halogens and the gaseous elements, usually require the vacuum ultraviolet region.

An example of the usefulness of this region dates back to 1936 when Harrison, successfully hurdling the high-vacuum obstacles, showed that selenium and sulfur could be determined in both nickel and steel. But it remained for the application of photoelectric detection to put these determinations on a routine basis. Applied Research Laboratories recently introduced the Quantovac, a

variation of the more familiar Quantometer, designed for photoelectric measurements mainly in the region 1600–2000A. The Quantovac may be flushed with dry nitrogen (transparent above 1600A) instead of being evacuated so that the high-vacuum problems are avoided. Table 1 gives the lines that are normally used for steel analysis.

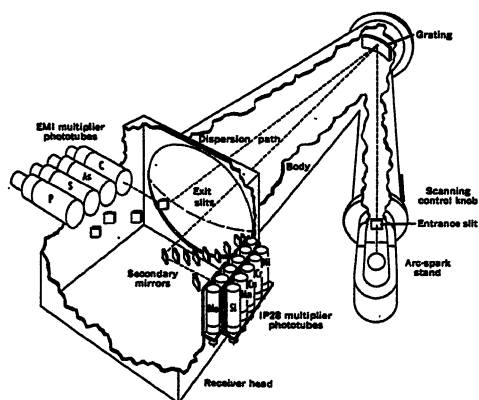
TABLE 1. QUANTOVAC (APPLIED RESEARCH LABORATORIES) STANDARD ARRANGEMENT OF MULTIPLIER PHOTOTUBES

1657A	Carbon	2714A	Iron
1783	Phosphorus	2933	Manganese
1820	Sulfur	3082	Aluminum
1890	Arsenic	3110	Vanadium
2316	Nickel	3133	Molybdenum
2516	Silicon	3175	Tin
2677	Chromium	3242	Titanium
		3274	Copper



(Courtesy Applied Research Laboratories, Inc.)

FIG. 2. Quantovac for determining carbon, sulfur and phosphorus in steels in addition to other alloying and "tramp" elements.



(Courtesy Applied Research Laboratories, Inc.)

FIG. 3. Optical arrangement of Quantovac. The phototubes for C, As, S and P are located inside the vacuum while those for the other elements are outside.

The Mond Nickel Co. Development and Research Laboratory in Birmingham, England, has made another compromise with the vacuum problem. Here a permanently evacuated spectrograph is used, the arc-spark stand alone flushed with nitrogen. With this arrangement, only a very short nitrogen path is introduced. K. M. Bills of the Mond Nickel Company reported that, using this instrument, 40 samples per day of cast iron may be analyzed for sulfur and phosphorus. Photoelectric integration results in a limit of detection of 0.002 % for sulfur and 0.005 %

for phosphorus. At levels of around 0.02 % concentration, a precision of better than 10 % of the amounts present is obtained.

Hilger recently announced its Fluorite Vacuum Polychromator, also called the CPS Evaluator. It is an instrument functionally similar to the Quantovac, but based on the design of Bills. With it, Hilger claims satisfactory accuracy for determinations of carbon, phosphorus and sulfur in routine analyses of steels. The time required for determining all three elements in a particular steel sample is given as under two minutes, a factor of at least ten better than conventional wet-chemical methods².

Because of the increasing emphasis on the role of gases in metals, vacuum spectroscopy is certain to blossom. As instruments and techniques of analysis become available, these elements will gradually be added to chemical specifications. Further evidence of such progress is the development of vacuum melting and casting techniques. Produced free of entrapped or alloyed gases, metals have many improved properties in ductility, strength, porosity, corrosion resistance, etc. As is so often the case, the value of the end-product will necessitate developing techniques for controlling its quality. Vacuum metallurgy, in other words, is greatly encouraging the development of vacuum spectroscopy.



(Courtesy Hilger & Watts Ltd.)

FIG. 4. Fluorite Vacuum Polychromator or CPS Evaluator specially designed for determining carbon, sulfur and phosphorus in metals.

Research in Free Radicals

As has been pointed out, study of vacuum spectroscopy is intimately connected with the outer space program. Another broad area where vacuum spectroscopy is being put to great use is in free-radical research. So important is this field considered that an exhaustive three-year research study at the National Bureau of Standards is under way in which scientists throughout the world have been invited to participate.

Although free radicals were discovered in 1900 by Gomberg, knowledge concerning their eccentricities has lagged. Free radicals may be defined as molecules in which one of the atoms has one of its valences unoccupied. They thus exhibit a valence one less than normal, e.g., carbon appears tri- rather than quadrivalent. With a missing electron, a free radical has an *odd* number of electrons, giving

rise to, among other phenomena, characteristic absorption bands. The more stable and complex free radicals have been studied through their absorption in the near ultraviolet, but the simplest, least stable radicals absorb only in the vacuum ultraviolet where, because of technical difficulties, very limited studies have been conducted.

Most free radicals are extremely reactive, another property which has discouraged their study. Explosions and flames are examples of where free-radical reactions abound. Methods of observing the antics of free radicals have, nevertheless, been devised over the years. A famous one was worked out by Paneth and Hofedetz in 1929.³ In an evacuated tube, they decomposed tetramethyl lead by heat to form the methyl free radical. At some distance along the tube was placed a lead mirror in order that any free

methyl reaching the lead mirror would tarnish it. Thus, at distances close to the source of tetramethyl lead, methyl free radicals would react with the lead mirror. Increasing the distance, a point would be reached where no free radicals would have survived the journey and the lead mirror would remain shiny. Mean free path calculations gave these pioneers data on the half-lives of the methyl free radical and a method had at last been found for making such measurements.

All free radicals are not, however, so easy to track down, a fact still hampering research in this field. Over the years, other techniques have been devised, a notable one being the use of trapping the free radicals, as they are produced, on a surface cooled by liquid air. Here their life expectancy—and the chances for their study—are improved considerably.

Today, the state of the art of free radical study is such that most work is still in basic research. Since many free radicals absorb energy in the far ultraviolet, the best new approach at detection makes use of spectroscopy in this region. Herzberg and his colleagues at the National Research Council in Ottawa have worked out a brilliant scheme for producing and then running down the free radicals using flash photolysis and absorption in the far ultraviolet. First they form the free radicals with a flash lamp of extremely high intensity. Once produced, the free radicals pose for about a millisecond

before they vanish. During this time, a Lyman source is switched on and the sample, placed in a cell between this source and the spectrographic slit, absorbs radiation from the Lyman source, producing characteristic spectra of the free radicals formed by the flash source. This cycle, causing the spectra to be recorded only when the Lyman source is on, is repeated as often as required to produce good spectrograms of the material under observation.

Going one step further, Nelson of the Bell Telephone Laboratories, has designed a flash lamp using a sapphire envelope^{4, 5} which permits irradiation down to about 1450Å. In this region, a great deal more energy is available for producing free radicals (see Fig. 5).

We have stated that most of the current work on free radicals is basic. Unlike many basic research adventures, however, the rewards here can almost be predicted. For instance, a better understanding of free radical reactions is virtually certain to spark the development of superior plant processing reactions. Other possible fruits of free-radical study are exotic fuels which will utilize the reaction heats of free radicals. No longer confined to science fiction pages are suggestions that aircraft fuels of the future may be obtained from the very atmosphere through which the aircraft travels. We hear of "photonic" energy in which the energy is derived from light. Such energy is being utilized already by telephone companies for powering

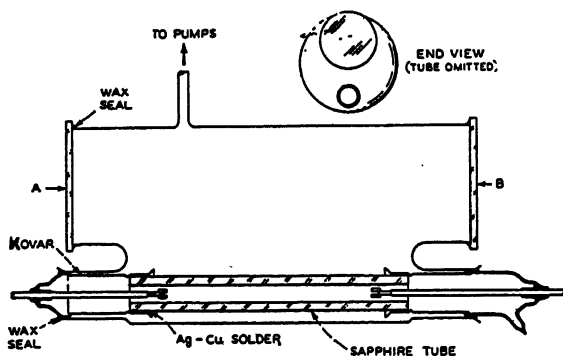


Fig. 5. Absorption cell used for flash photolysis experiments with a sapphire flash lamp.⁵

rural transmission lines. Another, even more exotic fuel, is ordinarily locked in unreacted atoms in our ionosphere. Thus the reaction mentioned earlier in which two free radicals of oxygen combine to form molecular oxygen offers energy for the taking. Will it be possible some day to utilize as a fuel the very same energy which destroys most rockets and meteors as they enter our atmosphere from outer space?

Other Research Problems

One major research area has already been mentioned: the study of free radicals. Other types of problems are enumerated below:

- (1) Determination of absorption coefficient.
- (2) Photoelectric studies of metals.
- (3) Photoionization of gases.
- (4) Determination of ionization and excitation potentials and dissociation energies.
- (5) Excitation spectrum of phosphors.

A good deal of the work in these areas is highly theoretical, results advancing our knowledge of the nature of atoms and molecules. But, as so often happens, practical results often emerge unexpectedly. The discovery that sodium salicylate has a constant quantum efficiency is a good example. It stemmed from a systematic study of the excitation spectrum of a great many phosphors.

The work on excitation potentials and dissociation energies has many ultimate goals. A better understanding of the mechanism of flames and explosions, for instance, may pave the way to more efficient fuels for jet and rocket aircraft.

Instrumentation

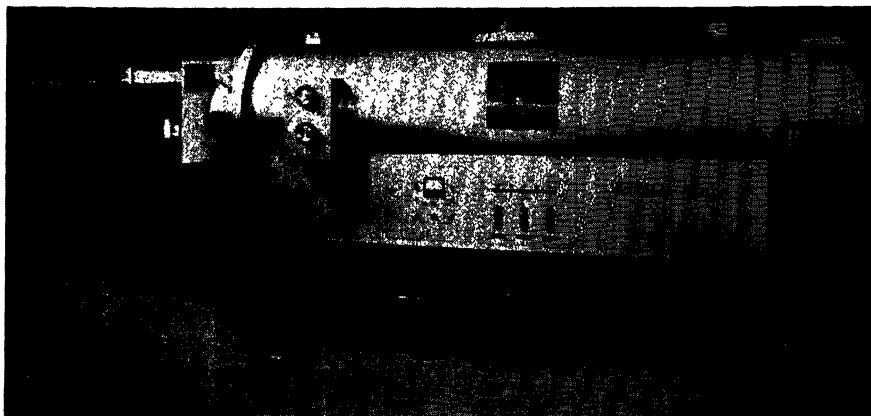
Already mentioned are two instruments designed for emission spectroscopy in the region above the fused quartz cut-off (around 1650Å). Between about 1100-1650Å is another region from the standpoint of instrumentation, a region where diffraction gratings may be used at normal incidence and still reflect a detectable amount of energy.

Below 1100Å, gratings must be used at grazing incidence for reflectivity. Mounts which employ grazing incidence are highly astigmatic and suffer from other optical imperfections. Urgently needed here is the discovery of a method of increasing the reflectivity of a grating at *normal* incidence. A recent paper by Haas and Tousey⁶ has shown a number of avenues by which this may be accomplished. An overcoat of magnesium fluoride over aluminum was found to increase its reflectance from 35 to 80 % at 1200Å and from 5 to 50 % at 1100Å. An evaporated film of platinum was found to have a reflectivity of about 20 % down to 600Å. Furthermore, platinum showed very little aging, being unaffected by intense far ultraviolet radiation. Zinc sulfide over germanium-coated glass was found to have a reflectivity of 20-35 % from 800 to 2000Å and has the advantage of very poor reflectivity in the near ultraviolet and visible. The advantage here is to cut down on spurious reflections from stray light.

For the region above 1100Å, several commercial instruments are now manufactured for absorption measurements particularly. Some are available in a so-called Seya mount in which wavelength changes are made simply by rotating the grating around its own axis; others have an automatic wavelength drive. Research instruments have been made using prisms as well as gratings in focal lengths up to 6.8 meters.

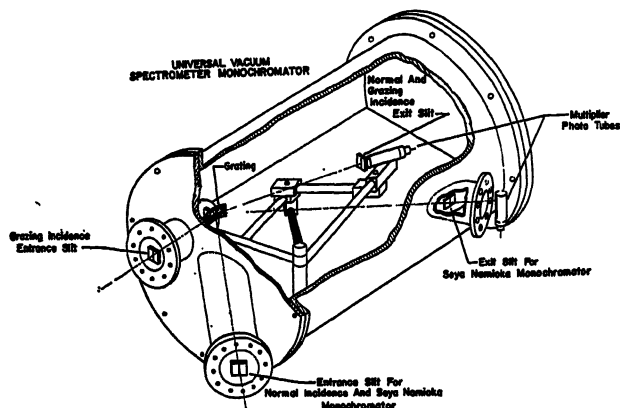
Despite the variety of instruments, much more work would be eagerly tackled if instrumentation were still more advanced. Outlined below are some of the problems which remain to be solved.

The Source. In absorption, the ideal source is a continuum of uniform intensity with wavelength in the region of interest. For the vacuum ultraviolet, no such constant source has yet been discovered. (The Lyman source leaves much to be desired.) Is it possible by employing the correct electrodes, the correct excitation and the correct



(Courtesy Jarrell-Ash Co.)

FIG. 6. Large research spectrograph for use in the vacuum ultraviolet region. The instrument employs a grating with a focal length of 6.8 meters.



(Courtesy Spex Industries, Inc.)

FIG. 7. Optical layout of instrument designed for use in grazing incidence region (below 1000Å) as well as region between 1000–2000Å. For the latter, a so-called Seya-Namioka mount is used in which, with the entrance slit kept at a fixed position ($70^{\circ} 15'$ with the grating), wavelength changes are simply made by rotating the grating.

atmosphere to devise such a source? If not, is it practical to combine several sources so that each will cover a particular region with a short overlap into the next? It goes without saying that the source or sources must be long-lived and foolproof, steady, without hazard and inexpensive.

Background. One of the severe optical problems in the vacuum ultraviolet is scattered light. We who are used to seeing crisp black lines on an otherwise clean plate are disappointed when we see our first grey-

on-grey far ultraviolet spectrum. The background results from scattered light reflected from blackened surfaces and the grating itself. Actually, the main trouble probably lies in the fact that aluminum (or sometimes platinum), used to coat the grating, reflects not much better than the baffles mounted in a vacuum spectrograph to prevent spurious reflections. Although aluminum is the best over-all reflector known, its reflectance drops from about 80 % at 2000Å to 25 % at 1200Å. Needed is a coating which may be applied to

gratings and mirrors to make them highly reflecting in the far ultraviolet.

Conveniences. Included in this category are all the vacuum controls, switches, gauges, safety devices, valves and bleeds which are presently necessary to understand and cope with in order to obtain vacuum spectra. Any contribution which reduces the complexity of the controls or eases the mind of the operator will greatly advance the art of vacuum spectroscopy. The operator must now be constantly on the alert lest a failure occur in the safety device protecting another safety device which, in turn, monitors the water flow to the diffusion pump.

Electronics. The improvements in related instruments are gradually overflowing into vacuum spectrographic instrumentation. Witness the Quantovac and the CPS Evaluator which use similar circuitry to that in other direct reading spectrographs made by ARL and Hilger.

There is no doubt that the far ultraviolet spectrum conceals a wealth of applications to be ferreted out some day. Rather than the occurrence of a breakthrough in technology, what is happening is that advances are being made slowly. Taken advantage of individually and compounded, they are gradually opening up this region to analytical techniques which would be otherwise impossible or impractical.

REFERENCES

1. JONES, L. C., JR., AND TAYLOR, J. W., *Anal. Chem.*, **27**, 228 (1955).
2. KELLY, J. H., *Canadian Min. and Met. Bull.* Nov. (1959).
3. PANETH, F., AND HOFEDETZ, W., *Ber.*, **62B**, 1337 (1929).
4. NELSON, L. S., *J.O.S.A.*, **46**, 768 (1956).
5. NELSON, L. S., AND RAMSEY, D. A., *J. Chem. Physics*, **25**, 372 (1956).
6. HAAS, G., AND TOUSEY, R., *J.O.S.A.*, **49**, 593 (1959).

A. J. MITTELDORF

X-RAY AND GAMMA-RAY ABSORPTION PHOTOMETRY (ABSORPTIOMETRY)

BASIC PRINCIPLES, INSTRUMENTATION AND APPLICATIONS*

Introduction

Today, 65 years after his momentous discovery of x-rays, it is easy to forget that Wilhelm Conrad Röntgen made the first observations on penetration and absorption of these rays and immediately instituted the first practical applications, which today are so well established in medical diagnosis, industrial radiography, microradiography, photometric analysis, gauging, absorption

spectroscopy, photochemical reactions, biological effects, and medical therapy. For all but the last three, direct observations of differential absorption is involved; for the last three it is clear that absorption of rays must precede chemical and biological changes. Röntgen and his contemporaries had only the measurements of absorption for evaluation of quality (or wavelength distribution) until the discovery in 1912 of diffraction by crystals. With this discovery absorption phenomena as such were eclipsed and in part nearly forgotten, while "shadowgraphs" of bones and tissues were taken more or less for granted. Within the past few years with the advent of such useful instruments as r-meters, phosphors, electron mul-

* Similar to a chapter by the same author in the revised edition of Vol. 1 of "Physical Methods of Analysis," edited by W. G. BURL, Academic Press, N. Y., 1960.

tiplier tubes, Geiger, proportional and scintillation counters, etc., there has been a re-awakening to the practical usefulness in many directions of observing absorption of x- and γ -ray beams in all types of materials. The ease and speed with which measurements can be made in comparison with other techniques has brought to the fore the analytical possibilities of absorptiometry or absorption photometry in academic and industrial laboratories. New automatic apparatus is on the market and many new applications are being found.^{16, 46, 47}

The Laws of Absorption

The absorption of x- and γ -rays follows the exponential equation

$$I_x = I_0 e^{-\mu x} \quad (1)$$

or

$$\frac{I_0}{I_x} = \exp[\mu x]; \quad \log \frac{I_0}{I_x} = \mu x \quad (2)$$

where I_x is the intensity of radiation of initial intensity I_0 , after passage through x centimeters of homogeneous matter, e is the natural base of logarithms, and μ is the linear absorption coefficient. If the beam of radiation has a cross section of 1 cm² then μ represents the fraction of energy absorbed per cubic centimeter of the absorber traversed. Because of a more frequent interest in absorption per gram instead of per cubic centimeter a more useful form of eq. (1) is

$$\frac{I_x}{I_0} = \exp [-\mu/\rho \cdot \rho x] \quad (3)$$

where ρ is the density of the absorbing layer and μ/ρ is the mass absorption coefficient, which is a simple function of atomic number and independent of physical state and temperature. The value of μ/ρ for a chemical compound is an additive function of the mass absorption coefficients of the constituent elements. Thus, in an example cited by Sproull,⁴⁶ x-rays passing from the ceiling to the floor of a room containing hydrogen and

oxygen may be 90% absorbed through the total height of gas, and on the floor there is 10% of the initial intensity. A spark is passed so as to cause combination to steam, without any change in absorption. When the steam is condensed to water, x-rays reaching the floor through the water or ice will also have 10% of initial intensity. For a given element μ/ρ increases with an increase in wavelength of the radiation absorbed, discontinuities appearing at the characteristic K, L, M, N, etc. absorption wavelengths (see "X-Ray Characteristic Absorption Spectrometry," p. 721). The μ/ρ values for many of the most important elements over a range of wavelengths are tabulated in the familiar handbooks of chemistry and physics.

The mechanism of the absorption process is shown by the fact that

$$\mu/\rho = \tau/\rho + \sigma/\rho \quad (4)$$

where τ/ρ is the true or fluorescent mass coefficient and σ/ρ is the coefficient due to scattering; μ/ρ is also a function of atomic number and of wavelength as shown by the equation

$$\mu/\rho = (CZ^4\lambda^3) N/A \quad (5)$$

where C is a constant over a range between characteristic absorption edges, Z the atomic number, λ the wavelength, N Avogadro's number, and A the atomic weight.

The laws of absorption apply to single wavelengths (or monochromatic beams) even though x-ray tubes generate a whole spectrum of rays. However, each such polychromatic beam has an "effective" wavelength, that is, the wavelength of a monochromatic beam absorbed to the same extent. X-ray absorptiometry is classified into two techniques, depending upon whether monochromatic or polychromatic beams are used.

Thickness Gauging

The exponential law indicates that absorption of a given x-ray beam of given intensity must vary with x , the thickness of

the homogeneous material. This suggests the simplest application of an absorption technique, namely, the evaluation of gauge and its constancy. Many materials occur in such shapes that micrometer thickness measurements are difficult or impossible. With an x- or γ -ray beam such determinations can be made without in any way touching the sample. It is necessary only to measure the diminution in initial intensity I_0 in passage through a layer. This may be done with a fluoroscopic screen or a photographic film, although only roughly since under the best conditions a difference in thickness of about 2% is required for visual differentiation of the blackening of the photographic emulsion. Still better is an ionization chamber or r-meter or Geiger counter, which can be made extremely sensitive so that a difference of the order of 0.1% is detectable. The logical practical equipment is a combination of phosphor and an electron-multiplier photoelectric tube first used for intensity measurement in 1942 by Morgan,⁵¹ for preliminary chemical analysis by Liebhafsky and Winslow⁴⁸ in 1945, and for rapid examination of fuses by Smith⁵⁵ in 1945. Operation with amplifiers and automatic continuous operation have followed.

During the war it became necessary to roll thin metal sheets of constant gauge, free from defects, for various types of precision equipment. At a constant voltage and current, x-rays could be passed through the sheet traveling at 800 feet per minute on the rolling mill. The unabsorbed radiation passes into an electron multiplier tube, the current in which is amplified to be read on an ammeter or otherwise arranged to signal when there is variation in gauge of the sheet. Variations in primary x-ray intensity are compensated by a null method since a beam from the opposite side of the target passes through a stationary sample of standard required gauge and then into another multiplier tube and the circuit linked with that registering absorption in the moving sheet. Deviations

from balance activate a Servo-mechanism which automatically readjusts the mill rolls more or less tightly.¹⁴ This technique of gauging is now established practice for a wide variety of rolled metal sheets. Continuous testing of deviations from concentricity of wire cores in insulation of high tension cables is now established practice.

Thin Coating Measurement

A very important measurement frequently required is that of the thickness of electroplated layers and coatings of all kinds. The methods depending upon capacitative or magnetic properties, or optical observations of reflectivity are often inadequate and difficult. Evaluation by x-ray absorption measurements has been found highly satisfactory in rapidity and simplicity. Several alternative techniques have been devised.

In the most sensitive and widely used techniques developed by Friedman and Birks²⁹ for measuring the thickness of single or multiple electroplated metal films, evaporated electrode coatings on piezoelectric crystals and thin pigment layers in the range from 10^{-5} to 10^{-2} cm, the x-ray source and detector are both situated on the same side of the coating. The x-rays pass through the coating and are reflected from the crystalline substrate at the proper Bragg angle from one of the principal sets of planes back to the detector, their intensity being reduced by absorption due to the double transmission through the coating. The commercially available focusing Geiger-counter powder diffractometers are used directly for this purpose. If t is the coating thickness, θ is the angle of incidence of the x-ray beam on crystal planes hkl in the substrate, and μ is the linear absorption coefficient $(\mu/\rho)\rho$ the ratio of the diffracted intensity from the coated specimen, I_t , to the intensity from the uncoated base material is:

$$\frac{I_t}{I_0} = \exp [-2\mu(t \sin \theta)] \quad (6)$$

Another important technique for measuring coating thickness depends upon excitation by primary x-rays of the characteristic fluorescent radiation of the substrate (see "X-Ray Emission Spectrometry," p. 726) and measurement of the attenuation in intensity in passing through the overlying coating. This method is satisfactory for determining the thickness over a range of 1 to 20 μ zinc on iron and steel with primary copper radiation. The substrate metal must have a lower atomic number than that of the coating in order to avoid interference from characteristic rays from the coating. It has been successfully used by Beeghly⁶ on tinplate; by Pellissier and Wicker⁵³ in the United States Steel Company laboratories; and by Zemany and Liebafsky⁵⁵ in the General Electric Company laboratories on attenuation by iron foil of characteristic lines from silver or zirconium substrates. Other methods which have had limited application are: (1) measurements of intensity ratios of two diffraction lines of the substrate with the x-ray primary beam perpendicular to the specimen, the values being dependent on preferred orientation and strain in the specimen; (2) measurement of intensity ratios by Gray³² and by Eisenstein²² of pairs of diffraction interferences from substrate and coating (a routine method for layers of SrO on BaO oxide cathodes), also subject to error from textural variations; (3) measurement of the absorption factor of the beam from an irradiated sample in aluminum foil, by which Gerold²¹ determined the thickness of a very thin chromium layer on brass with an intermediate nickel electrodeposited layer; (4) the method of Koh and Caugherty³⁹ for estimating the thickness of very thin coatings from the intensity of a characteristic line of the coating itself.

Porosity and Density Determinations

X-ray gauge methods are particularly useful on compressible materials such as leather, cellophane, cloth textiles, rubber blankets,

plastic films, paper, etc. It follows that porosity, as well as gauge, can be accurately determined, for x-rays measure only the true thickness of solid matter through which they pass without reference to free spaces and pores whereas only the apparent thickness is measurable by mechanical means such as micrometers. The porosity of the negative metallic lead plates in storage batteries as a function of temperature of formation and charging down to very low temperatures is an important factor, the capacity of the plates being determined by the penetration of sulfuric acid into the interior of the active mass. No possible mechanical measurement of the spongy mass could be made; but absorption of x-rays through sections of the plate of the same area and same mass of active material give the variations in thickness and porosity, the latter decreasing non-linearly with temperature and also with capacity of the plate.

A highly quantitative measurement of porosity of rubber-composition storage-battery separators has been made by Clark and Liu.¹⁸ This property is highly critical since sulfuric acid must diffuse through these separators which must insulate adjacent negative and positive plates from each other and prevent formation of lead trees. The average value (55 % porosity) compares very closely with the value derived from laborious pycnometric measurements, which cannot provide for closed pores unless the sample is powdered.

Recently x-ray absorption has been used in petroleum geology exploration to determine the porosity of sandstones, the oil saturation of drilling cores¹⁰ and related problems. Grohse³³ has found absorptiometry with polychromatic beams to be a unique method for studying the "fluidization" of a finely divided solid by a gas, as in beds of silicon fluidized by air. Bed density profiles which reveal the character and effectiveness of fluidization can be readily determined without disturbing the bed with internal

probes. Detonation waves,⁵⁸ boundary layers⁶¹ and density in supersonic flow, well suited for nozzle calibration⁶² are other applications of x-ray absorption.

Chemical Analysis From Absorptiometry

It is at once apparent that rapid chemical analysis can be made to depend upon differences in absorption of x-rays, for the concentration of one chemical element in the presence of others determines the difference in absorption between a sample and a reference. In 1929 Aborn and Brown¹ used x-ray apparatus with an ionization chamber to analyze gasoline for lead tetraethyl content, utilizing the large difference in mass absorption coefficients of carbon and hydrogen in gasoline and the lead. It was possible to achieve an accuracy of one part in 14,000.

In 1946 Sullivan and Friedman⁵⁷ successfully utilized a Geiger counter for x-ray absorption measurements for this same analysis of lead tetraethyl in gasoline. As shown in eq. (5) the mass absorption coefficient increases as the cube of the wavelength. In a single-component system it is logical to employ the longest wavelength transmitted by the sample, thus obtaining a maximum change in intensity for a given change in sample thickness. However, leaded gasoline is a two-component system in which the μ/ρ values change at different rates as the wavelength is varied. Hence an optimum wavelength generated at 17 kv is used with an absorption cell length of 15–25 cm. A counter tube filled with krypton is designed such that 80 % of the x-ray beam so generated is absorbed; or 80 out of 100 quanta entering the counter produce counts. At comparable sensitivity of the photomultiplier tube, the counter registered over 1000 counts per second. Standard deviation was 0.05 ml of lead tetraethyl per gallon of gasoline, or 1 %. Similarly a precision of 1 % was obtained with samples containing a maximum of 0.46 ml per gallon, corresponding to the

detection of 0.005 ml lead tetraethyl per gallon or 0.0002 % lead. The analysis can be made in one-tenth the time of any far less satisfactory chemical method.

In spite of the success of this analysis and the suggestion of many others applied to mixtures of gases, liquids, and solids no suitable equipment was placed on the market until late in 1946. The General Electric X-Ray Photometer among others is now in routine and research use for a wide variety of analytical problems.⁵⁴

The general arrangement is illustrated in Fig. 1. A tungsten target x-ray tube with beryllium window is operated at 15 to 45 kv. and 1 to 20 milliamps. with an enclosed power unit. Above the x-ray unit is a synchronous motor-driven chopper which alternately interrupts one-half of the x-ray beam after the other. A variable-thickness aluminum attenuator is placed above the chopper in one beam. Duplicate sample tubes are placed in the two beams above the attenuator. Sample cells up to 25 inches long can be accommodated; those for liquids and gases are arranged for continuous flow of the sample. Both halves of the beam fall on a common fluorescent screen protected from visible light by a thin metallic filter. An electron-multiplier phototube with associated power supply and amplifier determines when the beams are of equal intensity.

In operation a reference sample is placed in the cell above the attenuator and the unknown in the other sample tube. The attenuator is adjusted until the balance indicator shows that the two beams are of equal intensity; this position indicates a certain thickness of aluminum, which is equal in absorption to the difference between the reference sample and the unknown. Prior calibration enables an immediate determination in terms of the amount of impurity or solute in the unknown. The instrument may operate automatically to indicate or record this result directly. The exploratory work leading to the development of this successful com-

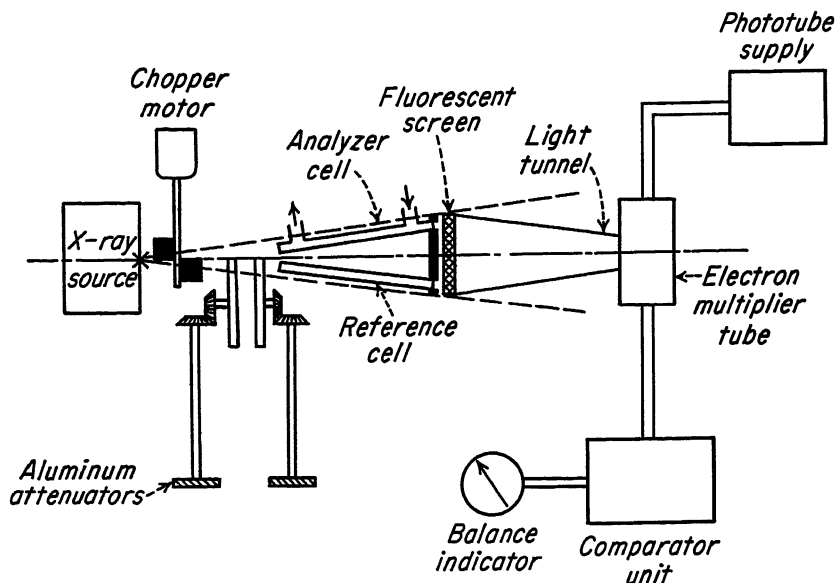


FIG. 1. Typical x-ray absorption photometer (absorptiometer).

mercial equipment was done by Liebhaufsky and associates^{46, 48} for solids, liquids, and gases under simplest conditions. The relation between x-ray absorption and two masses (m_1 and m_2) of sample is:

$$\log [I_1/I_2] = [i_1/i_2] = k(m_2 - m_1) \quad (7)$$

where I_0 and I_2 are intensities of x-ray beams transmitted, i_1 and i_2 are corresponding average output currents (from the phototube) and k is a proportionality factor. With a monochromatic beam

$$\log I_0/I = \log i_0/i = km \quad (8)$$

where I_0 and i_0 refer to the empty cell. With the commonly used polychromatic beam from a tungsten target tube, k varies inversely with m . It is defined by

$$\mu/\rho = 2.303ak \quad (9)$$

where a is the cross-sectional area of a cell containing m grams of sample; as already indicated μ/ρ varies with λ^3 , and the value of $\lambda_{\text{effective}}$ changes by absorption of the longer wavelengths. For quantitative analysis the effective wavelength must be deter-

mined for various thicknesses in order to determine μ/ρ in turn.

The analysis of gases is particularly interesting and significant. The equation used is

$$2.303 \log i_0/i = \mu_m pl \quad (10)$$

where μ_m is the mass absorption coefficient, ρ is the gas density, and l is the cell length in centimeters. Long wavelengths make possible a ratio of 6000 to 1 between output for hydrogen and chlorine.

The following examples of actual analyses for which the absorption photometer is employed are typical of an almost endless list of possibilities.

(1) Characterization of plastics (for use in cell windows, all lying between beryllium and aluminum).⁴⁶

(2) Sulfur content of crude and refined oil. A quantitative study leading to routine commercial analyses is that of Levine and Okamoto.⁴⁴ The equation

$$\ln (I_{\text{CHS}}/I_{\text{CH}} = (\mu_{\text{S}}' - \mu_{\text{CH}})\rho_{\text{CHS}}XF_{\text{S}} ,$$

where I is the intensity of the x-ray beam after passing, respectively, through the S-containing petroleum hydrocarbon (CHS)

and a pure hydrocarbon (CH, represented by calibrated polystyrene rods), μ' is the mass-absorption coefficient (for S and CH), ρ_{CHS} is the petroleum density, X is the length of the absorber, and F_s is the mass fraction of S in the C—H base (to be determined). Accuracy of analysis is ± 0.02 per cent S; one operator can analyze 30 samples per day, much faster and more economically than by chemical means and with comparable accuracy, together with nondestruction of samples.

A number of other absorption measurements of sulfur have been reported.^{21, 37, 52} Of particular interest is the K-capture determination of sulfur in hydrocarbons by the absorption of rays from iron-55. In this isotope (half-life 2.94 years), one of the two S-electrons in the K-shell is captured by the nucleus, thereby transmuting the atom into the next lower atom in the periodic table, in this case manganese-55. In the process of filling the K-vacancy, the K_α and K_β rays with a weighted wavelength of 2.07 Å are generated. Sulfur in the range 0.05 to 2.7% is easily and quickly determined by this essentially monochromatic absorptiometry, and is in routine use in the Socony-Vacuum Laboratories.

Other analyses may be made similarly with this isotope or Ni-59, Rh-102 or Cd-109 which are engaged in K-capture. Hughes and Wilczewski³⁵ have compared speed, accuracy and cost for sulfur determinations as follows:

Method	Speed			Rel. Cost		
	Elapsed time hr.	Operator time min.	Samples per day	Accuracy S %	Equipment	Operator time
Bomb Sulfur	24	36	13	0.003–0.14	5	7.2
Lamp Sulfur	3	29	16	0.03	1	5.8
X-ray Absorption (old K)	0.12	7	48	0.09	20	1.4
K-capture	0.08	5	60	0.05	6	1.0

(3) Quantitative "titration" of sulphydryl (HS) groups. This extremely important

analysis is carried out by assessing the amount of silver which can react with HS groups in proteins.

(4) Tetraethyl lead content of gasoline. Since the appearance of the photometer other critical investigations have been made of the x-ray absorption method of analysis for tetraethyl lead and reported in a symposium devoted entirely to the subject. Calingaert, Lamb, Miller, and Noakes¹⁸ improved accuracy by reducing primary-voltage fluctuation on the x-ray tube to ± 0.10 and further reduced sensitivity of the measurements of such fluctuations by a factor of 10 by introducing a polystyrene block in the reference beam. These authors found the method sensitive to 0.01 ml of tetraethyl/gal and the precision ± 0.01 ml for known gasoline-base stocks. The varying percentage of sulfur in gasoline was the chief obstacle to more accurate determination. Hughes and Hochgesang³⁴ found further advantage in using monochromatic radiation (preferably thorium lines near a lead absorption discontinuity, but for practical routine purpose the molybdenum K_α doublet). The tetraethyl-lead fluid actually added to automotive gasoline consists of 61.48% PbEt₄, 17.86% C₂H₅Br₂, 18.81% C₂H₅Cl₂, 1.7% kerosene, and 0.124% dye, corresponding to 4.8% H, 26.7% C, 13.8% Cl, 15.4% Br, and 39.4% Pb; aviation mixture differs only in having 35.68% ethylene dibromide and no dichloride. A straight-line working curve derived from the usual mass absorption equation with Mo K_α -radiation is obtained by plotting $\log (P/P_0)$ or $\log (t/t_0)$ against $\rho(0.587 + 9.31f_s) + 0.0478C_t$, where P is the radiant power of the x-ray beam of initial power P_0 after passing through the sample in an 8-ml absorption cell ($4\frac{1}{8}$ in long) or t and t_0 are the corresponding times for a fixed Geiger count of 10,000, ρ is the density, f_s the weight of fraction of sulfur, and C_t the concentration of tetraethyl lead in milliliters per gallon. When the sulfur content is known, an exact correction is made; otherwise an

X-RAY AND GAMMA-RAY ABSORPTION PHOTOMETRY

average value accepted by the ASTM of 0.064 per cent gives a satisfactory result.

It is interesting to compare accepted methods of tetraethyl lead analysis. The saving in personnel time of the x-ray over the chemical method pays the equipment cost every 6 months or in comparison with polarographic analyses every 8 months. Another x-ray method of analysis, by utilization of the intensity of the characteristic fluorescence spectrum for determination of lead and bromine, has been widely used (see "X-Ray Emission Spectrometry," p. 726). A Geiger count of only 1 minute at the peak of the L_{α} line of lead gave a probable error of ± 0.06 ml/gal of gasoline and for the Br K_{α} line of ± 0.16 ml/gal. Chlorine, sulfur, and other elements have negligible effect. Thus accuracy and speed are comparable with those of the x-ray absorption technique.

(5) Control of constancy of metal composition of metallo-organic compounds.⁶⁰

(6) Additives in heavy-duty lubricating oils (60).

(7) Ash content and quality of coal.

(8) Heavy-metal content of glass.

(9) Chlorine or fluorine content of polymers and plastics. Here values of μ/ρ are $H = 0.435$ (independent of wavelength), $C = 0.567$, $Cl = 12.0$, etc.

(10) Bromine content in gaseous brominated derivatives.

(11) Determination of formula of organic compound (C, H, O). Typical results are as follows:

	μ/ρ (measured)	μ/ρ (calculated)	Formula (experimental)	Formula (true)
Methyl alcohol	0.869	0.867	$CH_2O_{1.01}H$	CH_3OH
Acetone	0.734	0.728	$(CH_3)_2CO_{1.0}$	$(CH_3)_2CO$
Sucrose	0.869	0.884	$C_{12}H_{22}O_{10.8}$	$C_{12}H_{22}O_{11}$

At the Armour Research Foundation, an excellent method has been devised for determining the per cent composition of compounds composed of light elements,⁴ involving

determination of absorption by the unknown of monochromatic x-rays, excited by fluorescence, at several different wavelengths, and the subsequent solution of a series of simultaneous linear equations. For a compound composed solely of carbon, hydrogen and oxygen for example the beam attenuation is

$$I/I_0 = \exp \left[\left(-\frac{\mu_H}{\rho_H} \rho_H + \frac{\mu_O}{\rho_O} \rho_O + \frac{\mu_C}{\rho_C} \rho_C \right) X \right] \quad (11)$$

where μ/ρ 's are the mass absorption coefficients, ρ 's the element densities and X the sample thickness. At three different wavelengths the absorption coefficients for the three elements vary independently with wavelength. These equations for the three wavelengths are independent and can be solved for ρ_H , ρ_O and ρ_C as unknowns if μ 's are known and $\ln I_1/I_0$, $\ln I_2/I_0$ and $\ln I_3/I_0$ are experimentally determined. The characteristic radiations of Se, Rb and Zr were used in the analysis of solutions of ethanal and water with excellent agreement in percentage compositions with the theoretical values.

(12) Concentration of fillers and impregnants in wood, paper, cloth, rubber, carbon, etc. Titus⁵⁸ gives in comprehensive detail the quantitative analyses by absorptiometry with polychromatic beams of treated carbon brushes used in aircraft, this being the point-by-point exploration used for many materials. The treatment consists usually of impregnating the brush stock with a solution of a salt ($PbCl_2$, $CdCl_2$, BaF_2 , $BaBr_2$) to an extent that will leave the desired amount of chemical in the brush on water removal; the purpose of the treatment is to reduce or eliminate excessive wear of brushes used in motors and generators operating at high altitudes, by taking the place of adsorbed water vapor which ordinarily lubricates carbon brushes at sea level. In adjuvant type brushes a metal such as cadmium or MoS_2 is blended with carbon before pressing and graphitization. It is evident that there are

several types of carbon blanks which must be involved in making standard graphs, as well as the content and distribution of chemicals in the brushes. Once established x-ray absorptiometry becomes a rapid nondestructive production control method.

(13) Mineral content and efficiency of softening of water.

(14) Soil composition (qualitatively on account of complexity).

(15) Adsorbed contents of charcoals and silica gels.

(16) Concentration of reagent solutions containing metallic ions. The latest example is the determination of uranium in solution,⁶ a matter of the greatest importance in contemporary atomic-energy research. In the absence of contaminating elements the precision is ± 0.05 g/liter between limits of 0.1 to 10 g/liter. The presence of Na^+ , NH_4^+ , F^- , and other light ions had no effect, but heavier ions require separations. These solutions may also be analyzed as in the case of tetraethyl lead by fluorescence-spectrum analysis, which has the advantage of no interference by contaminating elements. In various Atomic Energy Commission reports by M. C. Lambert *et al.*, absorptiometry has been applied to aqueous solutions of 35 compounds and ions of 25 elements widely distributed in the periodic table. These extensive and precise absorbance data greatly facilitate absorptiometry with polychromatic beams.

(17) Alloy analysis especially when one alloying element is appreciably heavier than the base metal. For such an alloy, with a high atomic number element H and a low atomic element L , with weights respectively m_H and m_L g. cm^{-2} and mass absorption coefficients μ_H/ρ_H and μ_L/ρ_L the extinction or attenuation ($\log_e$ transmission) E of a monochromatic beam is

$$E = \frac{\mu_H}{\rho_H} \cdot m_H + \frac{\mu_L}{\rho_L} \cdot m_L \quad (12)$$

The influence of m is compared with the extinction from a standard made from H :

$$E_{\text{stand.}} = \frac{\mu_H}{\rho_H} \cdot m_{\text{standard}} \quad (13)$$

and a blank made from L

$$E_{\text{blank}} = \frac{\mu_L}{\rho_L} \cdot m_{\text{blank}} \quad (14)$$

This is the simple relation

$$m' = \frac{(E - E_{\text{blank}}) m_{\text{stand.}}}{E_{\text{standard}}} \quad (15)$$

permits calculation of the amount of the heavy element.²⁷

Histochemical Analysis

Absorption spectroscopic analysis has been perfected to the stage of a histochemical procedure, permitting the elementary chemical analysis of single mammalian cells. Absorption of monochromatic x-radiation is measured by ionization chambers, Geiger counters or photographically followed by microphotometry, for a series of wavelengths (isolated from primary or secondary fluorescent characteristic rays) lying on each side of a long wave absorption edge of the sought-for element. Thus it is possible to determine phosphorus and calcium in a 10μ -thick microtome section of a bony tissue within an area of $10 \times 10\mu$; nitrogen and oxygen within an area of $50\text{--}100\mu^2$ of a section 2μ thick. The actual weights are of the order of 10^{-9} – 10^{-12} g. Since such small localized areas may be examined the analysis may be directly correlated with the cytological picture. For these analyses the formula used is:

$$X = \frac{\ln(i_2/I_2) \cdot (\lambda_1/\lambda_2) - \ln(i_1/I_1)}{(\mu_1/\rho) - (\mu_2/\rho) (\lambda_1/\lambda_2)^2} \quad (16)$$

where X is the amount of the sought-for element in grams; the index 1 indicates the short-wave and 2 the long-wave side of the absorption edge for the element; I is the intensity of incident and i of transmitted rays; μ_1/ρ and μ_2/ρ mass absorption coefficients for

the element sought at wavelengths λ_1 and λ_2 ; and the exponent P may be found in tables.¹⁹ If λ_1 lies very near λ_2 , this reduces to

$$X = \frac{E_1 - E_2}{\frac{\mu_1}{\rho} - \frac{\mu_2}{\rho}} \cdot Y = \frac{E_1 - E_2}{R} Y \quad (17)$$

where $E_1 = -\ln i_1/I$ and $E_2 = -\ln i_2/I$; Y = area of analyzed surface. In the experiments for the determination of calcium (absorption edge 3.1 Å), the monochromatic beams had to be taken from a polychromatic beam of 7 kv; for phosphorus (absorption edge 5.8 Å), the $L\alpha_1$ line of niobium and the $L\beta_1$ line of zirconium; for nitrogen the K-absorption edge of 31.1 Å requiring high vacuum.

Similarly dry weights of cytological structures are determined with a filtered polychromatic beam of 1.5 kv peak, or 8.3 Å minimum wavelength. The analysis is done by a comparative method with a carefully prepared step gauge of nitrocellulose foils as standard, approximately the composition and absorbing power of proteins. Since the images representing differential absorption are photographically registered, enlarged and photometered, this is actually a quantitative application of microradiography. The total dry weight of individual ascites tumor cells, with a volume less than 4×10^{-9} cc, is found to be $3.95 \pm 0.20 \times 10^{-10}$ gram, agreeing with results of microchemical analyses of samples of many cells. Mucus- and enzyme-secreting cells have a greater mass (0.1×10^{-12} g/ μ^2) than acid-secreting. Extending these techniques Brattgard and Hyden²¹ obtained results on the mass, lipids (by chloroform extraction), pentose nucleoproteins (after digestion by crystalline ribonuclease), and residual cell proteins for various nerve cells—Deiters' cells and spinal ganglion and Purkinje cells, all of which are distinctly different in composition. This contribution to medical chemistry opens the way for many others.

Dichromography (in vivo Chemical Analysis)^{22a}

Obviously a nondestructive method for quantitative analysis of elements inside a living person would be of great value for determining the function of organs in diagnostic and physiological organs. This goal has been achieved in the analysis of the distribution of iodine in a normal human thyroid. To the first approximation the human body is composed of soft tissue, bone salt and iodine (in the thyroid or employed as a roentgenological contrast medium). If bone structures are avoided two x-ray wavelengths are therefore sufficient for an *in vivo* analysis of amount of iodine and soft tissue in a body section. The two wavelengths are chosen on each side of the K absorption edge of iodine at 0.37 Å. The equipment consists of a source of monochromatic fluorescent x-rays, two servo-controlled absorption wedges, a scintillator photomultiplier unit sensing the x-ray intensity, and an electronic feedback trap from the multiplier to two servo-motors. One wedge is composed of material equivalent in attenuating power for x-rays to soft tissue (water), and the other is iodine. When the patient is placed in the beam the two wedges are withdrawn a certain distance corresponding to the amount of soft tissue and iodine, the displacements being quantitative measures of amounts of each. A scanning process leads to quantitative distribution over a whole thyroid gland. The accuracy is better than ± 0.2 mg of iodine per cm^2 ; the chief error is due to the presence of fat, 1 gram being equivalent to 0.5 mg iodine. The soft tissue wedge is an additional protection so that the dose to the patient in a thyroid analysis is less than 1 mr. A stereogram of iodine distribution in a normal thyroid shows a peak concentration of 4 mg per cm^2 in the gland isthmus, and a total amount of 23.5 mg. The test for thyroid function is entirely different from that employed by introduction of radioactive iodine. The method is also useful for function tests

of liver, kidneys and lungs after intravenous injection of contrast substances containing iodine (for diagnostic radiography); for the amounts of blood in certain parts of the body; and with three selected wavelengths and three wedges the simultaneous determination of bone salt (trichromography).

γ -Ray Absorptiometry

Since γ -rays are formed in nuclear processes which generally involve high energies, the wavelengths are shorter than those of x-rays generated by conventional means, and the mass absorption coefficients are appreciably smaller than those encountered ordinarily in x-ray absorptiometry. Of course x-rays generated by resonance transformers, van de Graaff electrostatic generator and betatrons with energies of 1 mev or above overlap the γ -ray range, or even extend beyond it at $\frac{1}{2}$ -1 bev. Coefficients for γ -rays vary very much less from element to element in comparison with x-rays at 0.1 mev (100 kv) or less, so that the latter have the advantage in absorptiometric analyses. Actually the absorption characteristics of γ -rays (or x-rays in the same energy range) are very complex, because of entrance of the process of pair production. The net result is that the values of μ/ρ , instead of linearly decreasing with increase in radiation energy, level off to a nearly constant value, depending on the absorbing material, which means that absolute sensitivity is obtained—that is, thick and thin sections are penetrated nearly alike, and radiographs are correctly exposed without screening thin sections to prevent overexposure. This absorption of γ -rays has its chief usefulness in thickness gauging and in radiography. The general process of γ -ray absorption is given by Bethe and Ashkin.⁹

Extensive data on γ -ray absorption coefficients are available because of the vitally important shielding problems in an atomic age. A large number of papers indicate rapid progress in nondestructive testing such as thickness gauging and radiography best done

by isotopes cobalt 60, tantalum 182, cesium 137, iridium 192 and thulium 170. Especially valuable are papers by Aebersold,² Brewer,¹² Garrett *et al.*,³⁰ Johnston *et al.*³⁶ and Untermyer,⁶⁰ Berman and Harris⁷ attained a precision of 0.01% in thickness measurements with cobalt 60. Leboeuf, Miller and Connally⁴¹ make a notable comparison of x-ray and γ -ray absorptiometry (including a mixture of americium and plutonium as source). The advantages of the latter are: extreme stability of source intensity; decreased instrument complexity and compact size; more nearly monoenergetic source; much wider range of photon energies —20 to 2000 kev; lower cost. The chief disadvantage is low intensity, so that up to 50 kev x-ray absorptiometry prevails. Bernhard and Chasck⁸ applied γ -ray absorptiometry successfully to the measurement of soil density, as an indication of great present and future potentialities.

Combined Absorption — Diffraction Technique for Quantitative Analyses

In 1948 Alexander and Klug³ devised a method for quantitative analysis of mixture from powder diffraction patterns without the use of internal standards. The method was further developed and simplified in the Canadian Occupational Health Laboratory by Leroux, Lennox and Kay.⁴³ The general theoretical equation is

$$X_1 = \left(\frac{I_1}{(I_1)_0} \right) \left(\frac{\mu_s^*}{\mu_1^*} \right) \quad (18)$$

where X_1 = the weight fraction of component 1; I_1 = integrated intensity diffracted by a sample with mass absorption coefficient $(\mu_s/\rho_s)\mu_s^*$; $(I_1)_0$ = integrated intensity diffracted by a sample with mass absorption coefficient μ_1^* comprised solely of component 1. This equation holds for a monochromatic x-ray beam but for a polychromatic beam the correct experimental expression for X , requires a correction in the form of an expo-

ment of 0.652 for the ratios, as the result of a very critical study by Lennox.⁴² This technique was originally developed for analysis of industrial dusts for quartz, responsible for silicosis, but it is also in routine use for routine analyses in such industries as ceramics, refractories, paint and cement.

Radiography and Fluoroscopy

It is scarcely necessary to indicate that medical diagnostic radiography and industrial radiography, the best known and most widely practiced application of both x- and γ -rays, are direct consequences of differential absorption of rays by matter of varying homogeneity, thickness and density. The shadowgraphs are observed either on the fluoroscopic screen or the photographic film. So many excellent treatises are available that a review here of techniques and results is unnecessary. Here the progress in equipment is spectacular, as may be judged from the following:

(1) X-ray tubes only 7 or 8 feet long to operate at 1 and 2 million volts.

(2) Resonance transformers with Freon gas insulation so efficient that with the tubes at the core, the entire equipment may be included in mobile units; greatly improved and compact van de Graaff electrostatic generators for operation at 2,000,000 volts.

(3) The betatron or electron accelerator, developed by Kerst at the University of Illinois, in which the accelerating "donut" is also the x-ray tube producing beams up to 350,000,000 volts, far transcending the penetrating power or minimum wavelengths of γ -rays; a successful Allis-Chalmers 20,000,000-volt unit scarcely larger than an office desk, for radiography of sections up to 12 inches or more; automatic and multiple radiography both with these supervoltage units and with γ -rays from radioactive sources for 36 or more specimens tested at one time by arrangement on a circle around the source. In such a case supervoltage x-rays have very largely replaced γ -radiography in

industry because of the several hundredfold reduction in exposure time.

(4) The Westinghouse surge generator making possible radiographic exposures in a millionth of a second, for instantaneous photographs of moving objects such as bullets and artillery shells. The contribution to the science of ballistics in the past war is incalculable.

(5) *Monochromatic Radiography*. The limitations in resolving power, or in the radiographic detection of extraordinarily fine detail, with an x-ray beam of many wavelengths is apparent. This has suggested a re-examination of the possibilities of monochromatic rays (isolated by a crystal or less perfectly by appropriate filters) as applied to other industrial problems and to medical diagnosis. Many examples are cited in a recent paper.¹⁵

(6) *Industrial Fluoroscopy*. While this application so far is secondary to medical diagnosis, it is growing rapidly since electronic intensification of images has greatly increased safety for the operators against overexposure—a prohibitive factor in earlier attempts to use the fluoroscope for rapid, continuous inspection of products ranging from ball bearings and contact points to grain for insect infestation, citrus fruit, and packaged fruits and meats. By electronic devices the images formed by very weak beams of x-rays are intensified on screens far removed from radiation exposure, and now permit automatic control of filling of ammunition shells, beverage bottles and cans. Processes of mixing, diffusion, precipitation and other reactions in chemical industries within opaque materials and vessels may be continuously observed and controlled. The viscosity of tooth pastes and other similar products is measured by fluoroscopic observation of the rate of fall of metal balls. Long hoped-for, industrial fluoroscopy is an accomplished fact and is growing rapidly in 1960 as the result of meeting a challenge to a successful instrumentation.

Microradiography and X-Ray Microscopy (cf. "Encyclopedia of Microscopy")

The use of monochromatic rays becomes more necessary the smaller the specimen. Since there are no lenses for magnification of x-rays, one must resort to photographic enlargement up to 300 or 400 diameters of radiographic images on very fine-grained photographic emulsion such as the Lippmann. This is the basis of microradiography, which complements ordinary photomicrography but is the representation of structure of a specimen in three dimensions rather than merely of a polished surface. Over many years attempts were made to perfect a microradiography with a polychromatic beam generated at very low voltages such as 4000-5000 volts. A new very compact unit for contact microradiography operating at 1-5 kv is produced by Philips especially for biological specimens and for microanalysis discussed previously. For these long waves there is a favorable difference in absorption coefficients for various elements in thin specimens; but here again the polychromatic beam, and the lack of penetration even though air presents difficulties. In 1939 the writer advocated the use of monochromatic beams from easily available x-ray diffraction tubes operated at 30,000 volts or more. The result has been a successful development of a useful science. Here the idea of selecting the proper wavelength for maximum differentiation of constituents arose.

As an example, the values of $\mu_2 - \mu_1$, the differences of two linear absorption coefficients for constituents of a binary alloy as a function of wavelength, can be plotted as ordinate against wavelength. Such a plot would show a peak representing the largest possible difference in absorbing power; consequently the proper monochromatic wavelength corresponds to this peak to permit maximum delineation of phases. By this method some of the most important alloys utilized in war materials, even 5- and 6-com-

ponent systems, have been successfully analyzed in terms of phase structures, micro-defects and porosity, and strain. Many illustrations of microradiography and other techniques of x-ray microscopy will be found in the companion "Encyclopedia of Microscopy." For very small biological specimens, tissues, impregnated wood, and other organic materials microradiography has been a logical and useful extension of more usual macro or 1:1 radiography. Thus a new branch of histology depends upon the absorption of x-rays in various areas of a section only a few thousandths of an inch thick. These sections also may be preferentially "stained," not with the dyes of microscopy, but with varying absorbents for x-rays.

Some tissues are particularly well adapted for microradiography. The follicles of the thyroid gland contain iodine and thus are opaque to x-rays; when the follicles are treated by acid, sodium nitrite, and chloroform to remove iodine, they become transparent. Epidermis shows absorbing layers, the basal layer that supplies nutrition to upper ones, and the outer densely packed keratinized layer. Sulfur is responsible for some opacity of intermediate layers; the cells show protoplasm fairly opaque, lighter nuclei and very dark nucleoli. The variation in opacity of cells has a further bearing on radiosensitivity, since the greater the absorption the greater the amount of energy liberated by roentgen rays. It is generally true that the most sensitive cells are the most absorbent.

Cancer tissue gives excellent microradiographic detail, such as keratotic and parakeratotic globes or rose-shaped cell nests in epidermal cancer.

Another microradiographic technique developed by Trillat¹⁵ makes use of the photoelectrons liberated by primary roentgen rays. Hard roentgen rays generated at 180 kv pass through the Lippmann photographic film, which is insensitive, and then impinge upon a specimen closely pressed against the film.

The liberated photoelectrons from the surface interact with the photographic emulsion and so produce a characteristic image, which may be enlarged. The specimen may be a photographic negative that may be reproduced exactly. Under these conditions the primary and the secondary fluorescent roentgen rays have negligible effects in comparison with the photoelectrons. In addition to this reflection technique, a transmission modification consists in the use of a thin lead foil as a generator of photoelectrons. The hard roentgen rays first pass through this foil, which is in contact with the specimen and this in turn with the film. Photoelectrons from the foil pass through the specimen and register the radiographic image on the film, which may be microradiographed with 4000-volt roentgen rays and give equally good differentiation with 180,000-volt rays that liberate the easily absorbed electrons.

It was inevitable that attempts should be made in microradiography and historadiography to avoid the limitations imposed in enlargements of contact images of graininess of photographic emulsions. The solution of this problem has taken two courses with very successful results.

(1) **Grainless medium.** From among various x-ray-sensitive substances which will show no structure even in electron microscope ranges of enlargement. Ladd, Hess and Ladd⁴⁰ found that faces of ammonium dichromate crystals, and some polymers such as polyvinyl films were most useful. In both cases the solubility of the medium changes in proportion to the amount of exposure to the x-ray beam, with the result that the microradiographic image can be etched into relief by suitable solvents. Anhydrous alcohols are used for developing the image on the dichromate crystals, and a 30 % solution of acetone in water the image on the plastic sheets, in which cross-linking between polymer molecules has resulted from absorption. A cast, thin enough to permit the passage of an electron beam is then made of the relief

surface with silicon monoxide, carbon or other materials generally used for making replicas for electron microscopy. This replica is shadow-cast with metal vapors directed at an angle to the surface and then examined in the electron microscope up to 200,000 diameters magnification.

(2) **X-ray microscopy.** In ordinary microradiography sharp images can be gained only by intimate contact between specimen and film because the x-ray beam has a finite size. It follows that if the x-rays were generated from a point source, it should be possible to place the photographic film at various distances from the specimen and thus obtain sharp-edged images inherently enlarged from the divergent beam through the specimen. Such a procedure originally developed by Cosslett and Nixon²⁰ is now an accomplished fact and the General Electric X-Ray Shadow Microscope is a commercially produced instrument. Electrons from a filament are collimated into an extremely fine beam by means of magnetic lenses such as make electron microscopy possible. This beam impinges upon a thin piece of tungsten foil in the envelope of this special tube, and generates an x-ray beam from this point focal spot. After transmission through the thin specimen the enlarged image is directly registered on photographic films at distances up to several feet. The success of this microscope especially with freeze-dried biological specimen of all types alloys, clays and minerals, fabrics and other materials is quite remarkable.

REFERENCES

1. ABORN, R. H., AND BROWN, R. H., *Ind. Eng. Chem., Anal. Ed.*, **1**, 26 (1929).
2. AEBERSOLD, P. C., *Nondestructive Testing*, **12**, No. 3, 19 (1954).
3. ALEXANDER, L., AND KLUG, H. P., *Anal. Chem.*, **20**, 886 (1948).
4. Armour Research Foundation, Final Report, Air Force Project A-070.
5. BARTLETT, T. W., *Anal. Chem.*, **23**, 705 (1951).
6. BEEGHLY, H. F., *J. Electrochem. Soc.*, **97**, 152 (1950).

7. BERMAN, A. I. AND HARRIS, J. N., *Rev. Sci. Inst.*, **25**, 21 (1954).
8. BERNHARD, R. K., AND CHASEK, M., *Nondestructive Testing*, **11**, No. 8, 17 (1953).
9. BETHE, H. A., AND ASHKIN, J., "Expl. Nuclear Physics" (Ségré), Wiley, New York, Vol. I, p. 304 (1953).
10. BOYER, R. L., MORGAN, F., AND MUSKAT, M., *Petrol. Technol.*, **10**, No. 1, Tech. Publ. 2124, 19 pp. (1947).
11. BRATTGARD, S. O., AND HYDEN, H., *Acta Radiol. Suppl.*, **94**, 48 pp. (1952); **39**, 494 (1953).
12. BREWER, D. E., *Iron Age*, **172**, No. 27, 80 (1953).
13. CALINGAERT, G., LAMB, F. W., MILLER, H. L. AND NOAKES, G. L., *Anal. Chem.*, **22**, 1238 (1950).
14. CLAPP, C. W., AND POHL, R. V., *Elec. Eng.*, **67**, 441 (1948).
15. CLARK, G. L., *Radiology*, **49**, 483 (1947).
16. CLARK, G. L., "Applied X-Rays," 4th ed., McGraw-Hill, New York, p. 961 (1955).
17. CLARK, G. L., *Ibid.*, p. 238.
18. CLARK, G. L. AND LIU, C. H., *Anal. Chem.*, **29** (in press) (1957).
19. COMPTON, A. H., AND ALLISON, S. K., "X-Rays in Theory and Experiment," 2nd ed., Van Nostrand, New York, p. 533 (1940).
20. COSSLETT, V. E., AND NIXON, W. C., *Proc. Roy. Soc. (London)*, **B140**, 442 (1952).
21. CRANSTON, R. W., MATTHEWS, F. W. H., AND EVANS, N. (Sunbury Method), *J. Inst. Petrol.*, **40**, 55 (1954).
22. EISENSTEIN, A., *J. Appl. Phys.*, **17**, 874 (1946).
23. ENGSTRÖM, A., *Acta Radiol. Suppl.*, **63**, 106 (1946).
24. ENGSTRÖM, A., *Biochim. et Biophys. Acta*, **1**, 428 (1947).
25. ENGSTRÖM, A., *Rev. Sci. Inst.*, **18**, 681 (1947).
26. ENGSTRÖM, A., AND CARLSTROM, D., *Svensk Kem. Tidsk.*, **67**, 107 (1955).
27. ENGSTRÖM, A., AND PARRISH, W., *Svensk Kem. Tidsk.*, **68**, 445 (1956).
28. ENGSTRÖM, A., AND WEGSTED, L., *Acta Chem. Scand.*, **3**, 1442 (1949).
29. FRIEDMAN, H., AND BIRKS, L. S., *Rev. Sci. Inst.*, **17**, 99 (1946).
30. GARRETT, C., MORRISON, A., AND RICE, G., *Am. Soc. Testing Mat. Sp. Tech. Publ.* **145**, 9 (1953).
31. GEROLD, V., *Z. angew. Physik*, **4**, 247 (1952).
32. GRAY, R. R., *Phys. Rev.*, **69**, 49 (1946).
33. GROHSE, E. W., *Am. Inst. Chem. Eng. J.*, **1**, 358 (1955).
34. HUGHES, H. K., AND HOCHGESANG, F. P., *Anal. Chem.*, **22**, 1248 (1950).
35. HUGHES, H. K., AND WILCZEWSKI, J. W., *Anal. Chem.*, **26**, 1889 (1954).
- 35a. JACOBSON, BERTIL, *Science*, **128**, 1346 (1958).
36. JOHNSTON, J. E., FAIRES, R. A., AND MILLE, H. R. J., *Proc. 2nd Radioisotope Conf.*, Oxford, July, 1954.
37. KEHL, W. L., AND HART, J. C., *Proc. Am. Petrol. Inst.*, **III**, **23**, 9 (1948).
38. KISTIAKOWSKY, G. B., *J. Chem. Phys.*, **19**, 1611 (1951).
39. KOH, P. K., AND CAUGHERTY, B. J., *Appl. Phys.*, **23**, 427 (1952).
40. LADD, W. A., HESS, W. M., AND LADD, W. M., *Science*, **123**, 370 (1956).
41. LEBOEUF, M. B., MILLER, D. G., AND CONNALLY, R. E., *Nucleonics*, **12**, No. 8, 18 (1954).
42. LENNOX, D. H., *Anal. Chem.*, **29**, 766 (1957).
43. LEROUX, J., LENNOX, D. A., AND KAY, K., *Anal. Chem.*, **25**, 740 (1953).
44. LEVINE, S. W., AND OKAMOTO, A. H., *Anal. Chem.*, **23**, 699 (1951).
45. LIEBHAFSKY, H. A., *Anal. Chem.*, **21**, 17 (1949); **22**, 15 (1950); **23**, 14 (1951).
46. LIEBHAFSKY, H. A., SMITH, J. A., TANIS, H. E. AND WINSLOW, E. H., *Anal. Chem.*, **19**, 861 (1947).
47. LIEBHAFSKY, H. A., AND WINSLOW, E. H., *Anal. Chem.*, **28**, 583 (1956).
48. LIEBHAFSKY, H. A., AND WINSLOW, E. H., *Gen. Elec. Rev.*, **48**, 36 (1945).
49. LINDSTROM, B., *Acta Radiol. Suppl.*, **125** (1955).
50. LINDSTROM, B., AND MOBERGER, G., *Exptl. Cell. Research*, **9**, 68 (1955).
51. MORGAN, R. H., *Am. J. Roentgenol. Radium Therapy*, **48**, 88 (1942).
52. MOTT LAU, A. Y., AND DRIESSENS, C. E., JR., *Anal. Chem.*, **24**, 1852 (1952).
53. PELLISSIER, G. E., AND WICKER, E. W., *Elec. Mfg.*, **49**, 124 (1952).
54. RICH, T. A., AND MICHEL, P. C., *Gen. Elec. Rev.*, **50**, 45 (1947).
55. SMITH, H. M., *Gen. Elec. Rev.*, **48**, No. 3, 13 (1945).
56. SPROUL, W. T., "X-Rays in Practice," McGraw-Hill, New York, p. 72 1946.
57. SULLIVAN, M. V., AND FRIEDMAN, H., *Ind. Eng. Chem. Anal. Ed.*, **18**, 304 (1946).
58. TITUS, A. C., *Power App. and Systems*, No. 14, 1160 (Oct., 1954); *Proc. 1957 Conf. on Carbon*, p. 613, Pergamon Press, London.
59. TRILLAT, J. J., *J. Appl. Phys.*, **19**, 844 (1948).
60. UNTERMYER, S., *Nucleonics*, **12**, No. 5, 35 (1954).
61. VOLLMAR, R. C., PATTERSON, E. E., AND

- PETRUZZELLI, P. A., *Anal. Chem.*, **21**, 1491 (1949).
62. WELTMANN, R. N., AND KUHN, P. W., *Mail. Adv. Comm. Aeronaut. Tech. Note* 3098 (1954).
63. WINKLER, EVA M., *J. Appl. Phys.*, **22**, 201 (1951).
64. WINSLOW, E. H., SMITH, H. M., TUNIS, H. E., AND LIEBHAFSKY, H. A., *Anal. Chem.*, **19**, 866 (1947).
65. ZEMANY, P. D., WINSLOW, E. H., POELLMITZ, G. S., AND LIEBHAFSKY, H. A., *Anal. Chem.*, **21**, 493 (1949).
66. ZEMANY, P. D., AND LIEBHAFSKY, H. A., **103**, 157 (1956).

GEORGE L. CLARK

K-CAPTURE SPECTROSCOPY

K-capture spectroscopy is a modification of the older and more general method of analysis by x-ray absorption (q.v.). A radionuclide which emits x-rays by the K-capture process is used as a source in place of the x-ray tube and accessory equipment found in the more conventional procedures. Advantages in cost and simplicity of equipment in manipulation and in homogeneity of radiation are achieved. Although the term K-capture spectroscopy has been applied only to the use of a K-capture source for x-ray absorption, it could logically be used for other possible spectroscopic applications.

K-capture is a type of nuclear reaction which over 100 radionuclides undergo. One of the two s-electrons in the innermost or K-shell of an atom is pulled out of its orbit and is captured by the nucleus. This changes a proton to a neutron in the nucleus and transmutes the atom into one of the same mass number but of one lower atomic number. The vacancy in the K-shell is then filled by another electron, most frequently from the L-shell but also to a lesser extent from the M-shell, and the excess energy is emitted as the characteristic $K\alpha$ and $K\beta$ x-rays of the newly formed element. Thus, iron-55, which was the first radionuclide to be used in K-capture spectroscopy, forms manganese-55 which emits x-rays with a weighted

wavelength of 2.07 Å for the $K\alpha$ and $K\beta$ lines.

The general principles of x-ray absorption analysis apply also to K-capture spectroscopy and will not be discussed in this article except insofar as they have a bearing on the use of K-capture radionuclides as sources of x-rays for x-ray absorption analysis.

To be most useful as a source, a radionuclide should preferably emit no radiation, such as gamma rays or beta particles, other than the essentially monoenergetic x-rays produced by K-capture. However, it is possible in practice to use a source emitting some high-energy gamma radiation, since its absorption in the sample could be small and it could, additionally, be included in the background correction. Low-energy beta particles might be eliminated by absorption in the source. A useful radionuclide should also have a reasonably long half-life; it should be available at a reasonable price; and it should lend itself to the preparation of a convenient source.

By perusing a chart of nuclides, it is possible to pick out some three dozen radionuclides which decay with little or no emission of radiation other than K-capture x-rays. Many more emit other radiation in addition to x-rays. Of pure K-capture nuclides other than iron-55, nickel-59 is available but very expensive, and the others are either not available or have half-lives which are too brief. It is reasonable to expect that others may be made available if there should be a demand for them. In addition, there are some available K-capture nuclides which do emit additional radiation but which might, nevertheless, be useful under some circumstances. These include vanadium-49, manganese-54, zinc-65, strontium-85, cadmium-109, tungsten-181 and gold-195.

The x-rays emitted by an element are absorbed only moderately by itself and by the elements located closely above it in the periodic table, but quite strongly by those

located somewhat below it. This is illustrated by Figure 1¹ in which the mass absorption coefficients of some elements above and below manganese in atomic number are plotted. The absorption-edge effect is illustrated in this figure. The absorption relationships can be used as a guide in predicting the usefulness of the iron-55 source for the determination of a particular element in the presence of others. It should be possible, for example, to determine calcium in the presence of manganese, or sulfur or chlorine in the presence of carbon, hydrogen and oxygen. On the other hand, chlorine could not be determined in the presence of sulfur, or vice versa. By extending the curve to elements of higher atomic numbers other possibilities will appear.

Known pure K-capture radionuclides emit x-rays that cover a range of wavelengths from about 0.13Å to 4.7Å. For any particular radionuclide other than iron-55, the absorption edge shown in Figure 1 would be shifted either to the right or to the left. By

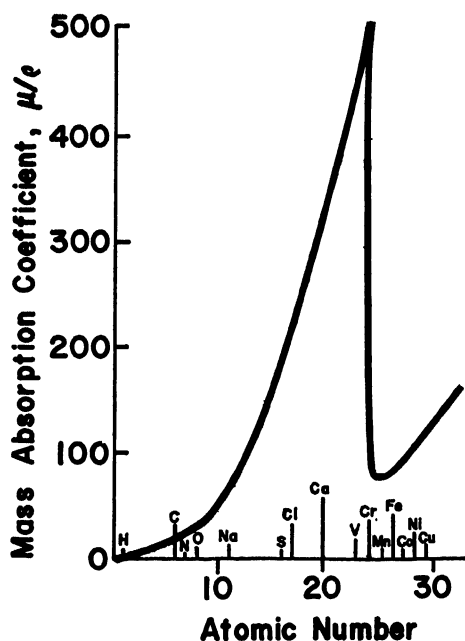


FIG. 1. Mass absorptivity of elements for iron-55 K-capture x-ray.¹

TABLE 1. SOME K-CAPTURE RADIONUCLIDES¹

Atomic Number	Element	K Wavelength (Å)	Atomic Numbers Strongly Absorbing
23	V	2.75	12-21
25	Mn	2.29	14-22
26	Fe	2.10	15-23
28	Ni	1.79	19-26
30	Zn	1.54	21-28

suitable choice of a source one could thus provide for the determination of a variety of elements in many compositions of matter.

The possibilities may be increased even more by using two sources for an analysis. Table 1¹ gives a list of five K-capture radionuclides (some also emit gamma rays) with the wavelengths of the emitted x-rays and the atomic numbers of the elements that absorb them strongly. The possibility of determining an element in a group of those absorbing strongly, in the presence of others in the group, would not be good. However, the considerable overlap in the strongly-absorbing elements from one group to the next, taken together with the absorption-edge effect, offer possibilities for specific analyses. Thus, for example, by the use of two sources, manganese-54 and iron-55, a specific method for vanadium might be devised. Vanadium, of atomic number 23, has a low absorption for manganese-54 radiation and a high absorption for iron-55 radiation. It could, therefore, be determined by the difference in the absorption of the rays from the two sources.

K-capture x-ray absorption may obviously be used to determine a highly absorptive element in the presence of elements of low absorption. It may also be used to determine a highly absorptive element in the presence of other highly absorptive elements provided the concentrations of the latter remain constant from sample to sample. But even in the first category, constancy of composition of the matrix is necessary to the extent required by the desired accuracy. Of course,

even two or more strongly absorbing elements may be determined together if they are always present in constant proportions to one another.

The equipment required consists of the source, a sample holder, a radiation detector, a standard absorber, and a recorder, such as a ratemeter, or a scaler and register with a preset timer or counter.²

The original instrumentation² was devised for the analysis of liquid samples, specifically for the determination of sulfur in petroleum hydrocarbons. The source consists of iron-55 plated on the end of a brass rod, enclosed in a metallic holder, fitted with a collimator and a shutter. The shutter opens automatically to allow the release of x-rays only when the cell holder is pushed into place. The cell is a chamber with beryllium windows. The transmitted x-rays are detected by a Geiger counter and counted on a scaler with a register and a preset counter. Such an instrument is available commercially. This instrument was later modified³ so that solid samples could be analyzed directly. (A preset timer was used instead of a preset counter.) A definite weight of solid sample is pressed into a flat disk and inserted into a slot in front of the shutter on the source holder. The rest of the instrumentation is similar to that first used except that a cell to contain liquid samples and a cell holder are not needed. A third type of instrument⁴ has been described for carrying out analyses on plant streams. This incorporates features designed to afford good fluid flow, ease of cleaning, pressure tightness to 50 psig, extreme compactness and inherent shielding.

Iron-55 may be obtained as a product of the nuclear pile by the reaction $\text{Fe}^{54} (n, \gamma) \text{Fe}^{55}$, starting with iron enriched with iron-54. It is a pure K-capture isotope, emitting no beta particles or gamma rays. However, if obtained as indicated, it is accompanied by iron-59 which emits beta and gamma rays, because of the presence of iron-58 in the target. This undergoes the

reaction $\text{Fe}^{58} (n, \gamma) \text{Fe}^{59}$. Fortunately, iron-59 has a half-life of 45.1 days whereas that of iron-55 is 2.94 years, so that by allowing the source to decay, a fairly pure iron-55 source is obtained. Iron-55 may also be purchased which is prepared in an accelerator from manganese-55 (present in an abundance of 100 % in natural manganese) by either of the reactions $\text{Mn}^{55} (d, 2n) \text{Fe}^{55}$ or $\text{Mn}^{55} (p, n) \text{Fe}^{55}$. Such a preparation, having no iron-59, is a pure K-capture nuclide. For use as a source, the radionuclide is plated out on the end of a brass rod and is protected with a thin coating of platinum. The metallic housing in which the rod is kept serves as sufficient shielding to avoid any radiation hazard. The apparatus is so arranged that the shutter cannot be opened to allow x-rays to emerge without automatically interposing a barrier to radiation in all directions except through the Geiger tube or other detector.

The intensity of the unobstructed source is too great to allow its transmission to serve as the reference value for calculating the relative transmittancy of samples. The reference value is therefore always measured by interposing between the source and detector an aluminum absorber of a definite thickness which serves as the standard zero reference. It has been shown² that the values for the mass absorptivities of a number of elements calculated from data obtained with the collimated monoenergetic iron-55 source agree with published values obtained by more conventional means. It should, therefore, be possible to calculate concentrations of a given element in a sample if the content of other elements in the sample is known. For petroleum hydrocarbons² one can, therefore, knowing the ratio of carbon to hydrogen in the sample, calculate values for sulfur which are not dependent upon calibrations obtained from sulfur values determined by other methods, such as lamp or bomb analyses. For routine determinations in petroleum products in the range 0.05 to 2.7 % sulfur, in a petroleum refinery laboratory, with ele-

ments other than carbon, hydrogen and sulfur absent in quantities above 0.01 %, sulfur may be determined with a reliability of about ± 0.05 % sulfur (twice the standard deviation).

For samples of more complex composition, one may determine a specific element by the use of an empirical calibration curve. In order to use such a curve successfully, one must know that the samples which are to be analyzed will vary essentially only in the concentration of the element to be determined. Variations in composition otherwise must be small enough to cause only negligible errors in the determination. For example, the solid-disk technique, with an iron-55 source, has been used for the routine, control determination of chlorine in plant samples of chlorobenzanthrone³ obtained during the progress of chlorination of benzanthrone. The calibration curve was based on chlorine values obtained by fusion of samples with sodium peroxide, followed by a Volhard titration for chloride. For samples ranging from 9.5 to 13.5 % chlorine, a standard deviation of the K-capture values from the values by chemical analysis was ± 0.23 % chlorine. This deviation comprises the errors of both methods.

The iron-55 source has also been used for

continuous analysis in the plant.¹ One application involved the determination of calcium present as a calcium soap dispersed in petroleum oil. Calcium and oxygen were present in a fixed ratio to each other and the sulfur content was constant for a given shipment of oil. The calibration curve was based on sulfated ash values. Another application was the monitoring for ammonium chloride of wash water which had removed that compound from a bubble-cap section of a scrubber tower. The ammonium chloride content dropped from 6 per cent to less than 0.1 per cent during the washing. Attainment of a predetermined concentration was signaled by the method as a point for stopping the washing operation.

These examples just touch upon the widespread possibilities for using this convenient and inexpensive method for many laboratory and plant analyses of standardized compositions of matter.

REFERENCES

1. BEERBOWER, Alan, *Control Engineering*, 6, 128 (1959).
2. HUGHES, HAROLD K, AND WILCZEWSKI, JOHN W., *Anal. Chem.*, 26, 1889 (1954).
3. SEAMAN, WILLIAM, LAWRENCE, H. C., AND CRAIG, H. C., *ibid.*, 29, 1631 (1957)

WILLIAM SEAMAN

X-RAY CHARACTERISTIC ABSORPTION SPECTROMETRY

Just as emission and absorption spectroscopic analyses in the optical ranges of the electromagnetic spectrum are such important instrumental techniques, so may characteristic x-ray emission lines and absorption edges be utilized by the chemist. It has long been known that each chemical element has one characteristic K absorption wavelength, 3L, 5M, 7N, etc., the relationship to atomic number being governed by Moseley's law.²

Thus when an absorbing screen is placed in the path of an x-ray beam, and the transmitted beam is analyzed with the crystal spectrometer, sharp discontinuities or edges in the continuous spectrum may be found corresponding to the characteristic absorption wavelengths in the various series for each element present, these being independent of physical state or chemical combination. The characteristic absorption wave

X-RAY CHARACTERISTIC ABSORPTION SPECTROMETRY

length is that at which a chemical element suddenly becomes much more transparent to an x-ray beam containing a continuous range of wave lengths.

The single K absorption edge (sometimes with a fine structure disclosed at high resolutions) has a wave length always about $\frac{1}{4}\%$ lower than that of the shortest $K\gamma$ emission line. The energy $h\nu_{Kabs} = hc/\lambda_{Kabs}$ characterizes the innermost K shell of electrons, and so represents the energy required just to lift a K electron out of the atom. The ionized atom with the K vacancy or in the K state returns to the normal state when electrons fall to the K level from L, M, and higher levels thus emitting the K spectrum. Thus the critical voltage on an x-ray tube for electron acceleration to the target and excitation of the K-series spectrum lines is $V_e = h\nu_{Kabs}$. The following wave lengths of the K series of tungsten illustrate the general relationship:

Kabs	0.17837 Å	
$K\gamma$	0.17935 (sometimes designated $K\beta_2$)	
$K\beta_1$	0.18463	} doublet
$K\beta_2$	0.185143	
$K\alpha_1$	0.208992	} doublet
$K\alpha_2$	0.213813	

Since the L electronic shell comprises 3 levels close together designated by the quantum numbers $2_{0,1/2}$, $2_{1,1/2}$ and $2_{1,3/2}$ there are 3 L absorption edges, and the more than 20 L emission lines can be generated in groups

by controlled voltage. The 5M edges have been measured for heavy elements, but there are few values for the theoretically possible 7N, 50 and 3P levels. Representative values for tungsten are:

L_I	1.0226
L_{II}	1.0736
L_{III}	1.2140
M_I	4.39
M_{II}	4.81
M_{III}	5.46
M_{IV}	6.63
M_V	6.86

Not a great deal of use in chemical analysis has been made of this particular technique over the years, probably because the emission spectra are somewhat more sensitive. The height of this edge or discontinuity evaluated with the modern spectrometer with sensitive detector near and on either side of the characteristic absorption edge is a quantitative measure of the amount of element is unknown. This is governed by the equation

$$\frac{I_2}{I_1} = e^{-cp}$$

where I_2 is the intensity of the radiation leaving the absorption screen on the short wavelength side of the discontinuity, and I_1 the intensity of the long-wave side; c is the coefficient which must be experimentally determined, and p is the amount of element present. In Table 1 are probably the best data available for values of c and m , the weight in milligrams per square centimeter for the production of an absorption edge with a 5% intensity difference in the two sides.

The method has been used successfully for analysis of barium in glass, antimony, barium, lanthanum, bismuth in alloys, and many others. A recent very successful application has been the determination of zinc and molybdenum¹ in liquid hydrocarbons, lead and bromine in engine combustion

TABLE 1

At. number	Element	c K edge	c L edge	m K edge	m L edge
42	Mo	69		0.7	
47	Ag	45		1.1	
50	Sn	34		1.5	
51	Sb	31		1.6	
56	Ba	24		2.1	
58	Ce	22.5		2.2	
74	W	8		6.0	
82	Pb	5.7		16.0	
90	Th		50		1.0
92	U		45		1.1

chamber deposits, molybdenum, nickel and platinum in solid sulfur. The method is independent of other elements present, specific and nondestructive. At higher concentrations this method is preferred to x-ray fluorescence (q.v.) because of the absence of a matrix effect; it is not as sensitive as fluorescence at the trace level. However, with the advent of Geiger spectrometers, and new x-ray tubes delivering extremely intense beams up to 5,500,000 roentgens per minute, many of the former difficulties are eliminated. It is easily possible to make analyses for elements as low in atomic number as potassium with present equipment, and to magnesium or below with special provisions parallel with progress in emission spectrometry.

The technique discussed in this article employs a *polychromatic* x-ray beam with a

continuous or "white" spectrum. A given chemical element in a specimen absorbs all rays with wave lengths shorter than the characteristic absorption wave length to a far greater extent than rays with longer wave length. A closely related method for analysis consists in the measurement in a specimen of *monochromatic* beams (isolated characteristic emission lines) with wave lengths just shorter and just longer than the characteristic absorption wave length of the element in question. This absorption technique is included in the article on X-Ray Absorption Photometry (Absorptiometry), p. 703.

REFERENCES

1. BARRIER, R. E., *Anal. Chem.*, **29**, 348 (1957).
2. CLARK, G. L., "Applied X-Rays," 4th ed., p. 113, McGraw-Hill, New York, 1955.

G. L. CLARK

X-RAY DIFFRACTION OR CRYSTAL SPECTRA

QUANTITATIVE ANALYSIS

X-ray diffraction analysis consists of comparing the diffraction pattern of a powdered sample containing an unknown amount of the component sought with the diffraction patterns of mixtures containing known amounts of the component sought. This technique is often used whenever rapid determinations, accurate to perhaps a few percent, are acceptable, or when chemical analyses are unreliable or even impossible. The determination of quartz in mine dusts was one of the first applications; in fact the development of quantitative techniques resulted largely from the excellent work done in regard to this problem by several workers beginning with Clark and Reynolds.⁹

Debye-Scherrer patterns may be recorded photographically in a conventional cylin-

dric camera or by using a diffractometer with a recorder. The measurement of intensities of diffraction lines is much simpler with the recording diffractometer than with the cylindrical camera, so the diffractometer has almost completely displaced the camera for quantitative analysis. For this reason in the discussion to follow it will be assumed that the diffraction patterns are obtained with the diffractometer.

Under certain conditions the equation relating the integrated intensity of diffracted x-rays to the absorptive properties of a sample is

$$I_{ij} = \frac{K_{ij}x_j}{\rho_j[x_j(\mu_j^* - \mu_m^*) + \mu_m^*]} \quad (1)$$

where

I_{ij} = intensity of i th line in the Debye-Scherrer Pattern of component j .

x_j = weight fraction of component j
(grams per gram of sample).

ρ_j = density of component j .

μ_j^* = mass absorption coefficient of component j .

μ_m^* = mass absorption coefficient of the matrix (the material that would remain if component j were removed).

K_{ij} = constant which depends upon the characteristics of the apparatus and upon the structure of component j .

The necessary conditions that Eq. (1) be valid are:

(1) The sample is a uniform mixture of particles small enough to make extinction and microabsorption effects negligible.^{7, 15}

(2) The sample thickness is such that the diffracted x-rays have maximum intensity.

(3) Porosities of samples must be the same for intensities to be compared.

(4) The crystallites must be randomly oriented.

The use of Eq. (1) will now be considered for three general cases: (1) Samples for which $\mu_j^* = \mu_m^*$; (2) two-component mixtures in which $\mu_j^* \neq \mu_m^*$; (3) mixtures of several components in which $\mu_j^* \neq \mu_m^*$, or in which μ_m^* is not known (the usual case).

Case 1: $\mu_j^* = \mu_m^*$. For this case Eq. (1) reduces to

$$I_{ij} = K'x_j \quad (2)$$

Direct analyses may be made by comparison of the diffraction pattern of the sample with that of the pure component, subject of course to the four conditions stated above. In those instances where the component sought has a strong cleavage plane it will be difficult to achieve a uniform porosity and random orientation simultaneously. One other condition should be added to those stated above when direct analyses are performed, namely, the x-ray beam intensity must be maintained at the same constant value for all patterns.

Case 2: Two-component mixtures where $\mu_j^* \neq \mu_m^*$. For this case the relationship between I_{ij} and x_j will not be linear, but direct analyses may still be made, subject of course to the five conditions stated above, by preparing a calibration curve from the diffraction patterns of mixtures with known compositions of the two components.

Case 3: Mixtures of several components in which $\mu_j^* \neq \mu_m^*$, or in which μ_m^* is unknown.

In this case Eq. (1) may be expressed:

$$I_{ij} = \frac{K_{ij}x_j}{\rho_j\mu_T^*} \quad (3)$$

where μ_T^* is the mass absorption coefficient of the sample.

The intensity of the k th line of another component l is

$$I_{kl} = \frac{K_{kl}x_l}{\rho_l\mu_T^*}$$

Because I_{ij} and I_{kl} are measured on the same sample, and μ_T^* is characteristic of this sample the ratio of these intensities is independent of μ_T^* :

$$\frac{I_{ij}}{I_{kl}} = \left(\frac{K_{ij}\rho_l}{K_{kl}\rho_j} \right) \frac{x_j}{x_l} = R_{kl}^i \frac{x_j}{x_l} \quad (4)$$

Equations 1-4 were first derived by Alexander and Klug.¹ Eq. (4) is the formula used by many investigators^{1, 5, 7, 8, 9, 11, 12, 13} and is the equation fundamental to the use of an internal standard. It eliminates the small errors due to micro-adsorption effects. Eq. (4) may be applied to quantitative analysis in two ways: (1) another substance, called an internal standard, may be added in a known proportion to the sample, or (2) the component sought itself may be added to the sample and the line of another component present used as the internal standard.¹⁰

1. *Addition of an Internal Standard.* When a known amount of component l is added to unit weight of the sample, the weight fraction of x_j is given by

$$x_j = \frac{x_j}{x_l} \cdot x_l = \frac{1}{R_{kl}^i} \frac{I_{ij}}{I_{kl}} x_l \quad (5)$$

where x_l is the weight of component l per unit weight of original sample, x_j is the weight of component j per unit weight of original sample.

For quantitative analysis a calibration curve is prepared from diffraction patterns of mixtures with known composition of the component sought and the internal standard. The ratio of intensities I_{ij}/I_{kl} is plotted as a function of the ratio of the weight of the component sought to that of the internal standard. A straight line passing through the origin is obtained.

2. *Addition of the Component Sought.* In some instances it may be more convenient to use one of the components present in the sample as the internal standard by adding a known weight, δ per unit weight of sample, and determining a second relative intensity (or perhaps several). Eq. (4) applied to this case becomes:

$$\frac{I_{ij}}{I_{kl}} = R_{kl}^{ij} \frac{(x_i + \delta)}{x_l} = C(x_i + \delta) \quad (6)$$

where $C = (R_{kl}^{ij}/x_l)$ is constant since the weight of component l per unit weight of original sample is unchanged. A plot of I_{ij}/I_{kl} as a function of δ , the weight of component j added per unit weight of original sample, is a straight line. The intercept at $\delta = 0$ is the relative intensity measured on the original sample. At $I_{ij}/I_{kl} = 0$, $x_j + \delta_j = 0$, consequently the quantity sought, x_j , is the absolute value of the δ axis intercept. Knowledge of the constant of proportionality R_{kl}^{ij} and of x_l is unnecessary, but intensity ratios for two or more values of δ must be determined.

Equations (5) and (6) are valid for all possible combinations of lines for the two components, consequently several estimates of x_j can be obtained, thus increasing the accuracy of the determination. The advantage of this procedure seems first to have been pointed out by Brentano.⁶ Sometimes the lines of component j may not be completely resolved from the lines of component

l . It is generally possible to correct for such superpositions¹⁰ as long as one line of the internal standard is free of superpositions.

It is also possible to analyze for several components in a single sample. Black⁵ describes a method for analyzing bauxite for several components. Copeland and Bragg¹⁰ discuss a general theory for setting up such analyses.

Precision of Analysis. The precision of the analysis depends upon (a) the precision of the intensity measurements and (b) the characteristics of the sample.

The precision of the intensity measurements is influenced by the random nature of x-ray emission, the stability of the x-ray generator (when using a diffractometer), and the characteristics of the counting devices used to detect the x-rays.

Bateman⁴ showed that the probability of x-ray emission had the Poisson distribution. A characteristic of this distribution is that its variance is equal to its mean. This is significant to x-ray analysis, for it means that in principle the relative error of an intensity measurement can be reduced to any desired level by waiting for a sufficiently large number of x-rays to be diffracted.

Geiger tubes, frequently used as the detecting device, have an insensitive or "dead" time. The observed count is thus increasingly in error as the x-ray intensity rises. Alexander, Kummer and Klug² discuss procedures for correcting this error.

The specifications the sample must meet to obtain precise intensity measurements are:

- (1) The sample must be finely ground; a particle size of not more than a few microns is desirable.
- (2) The sample must be thick enough to absorb all the incident x-rays (for diffractometer use).
- (3) Preferred orientation must be absent.
- (4) Extinction effects must be absent.
- (5) The sample must be stable during measurements.

X-RAY EMISSION SPECTROMETRY

Several investigators have described techniques for sample preparation that will meet these requirements.^{3, 11, 14} In practice the relative error of an analysis can be made less than 1% in favorable cases.

REFERENCES

1. ALEXANDER, L., KLUG, H. P., *Anal. Chem.*, **20**, 886 (1948).
2. ALEXANDER, L., KUMMER, E., KLUG, H. P., *J. Appl. Phys.*, **20**, 735 (1949).
3. BALLARD, J. W., OSHRY, H. I., SHRENK, H. H., *J. Opt. Soc. Am.*, **33**, 667 (1943).
4. BATEMAN, H., *Phil. Mag.*, **20**, 704 (1910).
5. BLACK, R. H., *Anal. Chem.*, **25**, 743 (1953).
6. BRENTANO, J. C. M., *J. Appl. Phys.*, **20**, 1215 (1949).
7. BRINDLEY, G. W., *Phil. Mag.*, **36**, 347 (1945).
8. CLARK, G. L., LORANGER, W. F., BODNAR, S. J., *Anal. Chem.*, **26**, 1413 (1954).
9. CLARK, G. L., REYNOLDS, D. H., *Ind. Eng. Chem., Anal. Ed.*, **8**, 36 (1936).
10. COPELAND, L. E., BRAGG, ROBERT H., *Anal. Chem.*, **30**, 196 (1958).
11. COPELAND, L. E., BRAGG, ROBERT H., A.S.T.M. Bull. No. **228**, 56 (1958).
12. DUWEC, P., ODELL, F., *J. Am. Ceram. Soc.*, **32**, 180 (1932).
13. KLUG, H. P., ALEXANDER, L., KUMMER, E., *Anal. Chem.*, **20**, 607 (1948).
14. SWANSON, H. E., FUYAT, RUTH E., Circular No. 539, Nat'l. Bur. Standards, (1953).
15. WILCHINSKY, Z. W., *Acta, Cryst.*, **4**, 1 (1951).

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X-RAY EMISSION SPECTROMETRY

ANALYTICAL APPLICATIONS (ESPECIALLY METALLURGICAL)

Analytical Advantages

Introduction. The use of an instrument for accurate chemical analyses depends entirely on the instrument's versatility and the economics of the method. Economics is the major criterion for production analytical laboratories. This can be summed up by two factors: time required for an analysis, and the actual materials and labor cost of the analysis. All points considered in this article will be based on how the metallurgical industry considers the problem.

Time. Time is most critical to production analyses when a heat of an alloy is being held in a furnace. A quick report on whether the alloy meets specifications can save the cost of a remelt. Most elements cannot be analyzed before a heat is poured, if all analyses are to be made by wet chemistry methods. The use of x-ray fluorescence spectrometry has changed a large portion of this picture. Chromium analysis time by wet

chemistry is at best 30 minutes. This does not include sample preparation time, and allows errors in the technique greater than ± 1 percent of the amount present. Putting this same sample through x-ray analysis by steps of sample preparation, comparison to standards, and calculation of the results, the answer with an accuracy of better than ± 0.5 percent of the amount present can be completed in 20 to 25 minutes. This is a comparison of quantitative analyses. All *qualitative* analyses by x-ray fluorescence can be made as quickly as the goniometer can be set on the characteristic 2θ angle and the sample inserted. A wet chemical analysis in some cases might take hours, and a chemical spot test could ruin a finished surface.

Materials and Labor. The second economic factor is cost of materials and labor for performing an analysis. Sample cost is approximately the same for x-ray and for wet chemical methods. A cast sample is made for either method.

Labor, which is the major operating cost, is cut from approximately two man-hours

per sample to an average 20 minutes per sample. The time gained comes totally from the difference in the method. Another factor to consider is the handling of rush jobs. Wet chemistry cannot be rushed without losing the value of accuracy. The x-ray fluorescence method, employing an electronic machine, will perform the analysis by several methods swiftly and accurately.

The most common methods for measuring quantitatively with x-ray spectrometer are:

(a) Use a constant number of counts and measure the time to register this number.

(b) Use a constant time and read the measured counts for this period of time. Either method is reduced to the number of counts per unit time, e.g., counts per second.

(c) Record the millivolt signal on a strip chart recorder and measure the peak minus background intensity of each element.

(d) Record the millivolt signal on a strip chart recorder and measure the area under a peak with a digital computer.

Methods (a) and (b) are the most common ways of x-ray fluorescence analysis. Method (d) is a recent addition to quantitative techniques.

Accuracy and Reproducibility of Results. A quick analysis does not always mean an accurate one. The accuracy of the results is determined by the method. Production requirements or tolerances dictate the method of analysis. A comparison of the fluorescence method of analysis against the wet chemistry method in Table 1 presents a picture of the relative accuracy for these two methods. More than one concentration level is shown for all of the elements except manganese and vanadium.

Results from the x-ray method, as applied, appear more accurate in almost all cases than those obtained by wet chemistry. The comparison is made of results from routine x-ray or routine wet analyses with the umpire wet chemistry analyses. The latter data are obtained by very tedious, accurate, wet chemi-

TABLE 1. COMPARISON OF X-RAY, ROUTINE WET, AND UMPIRE ANALYSES RESULTS

Element	X-Ray	Routine Wet	Umpire Wet	X-Ray % Error	Routine Wet % Error
% W	18.00	18.20	18.03	0.17	0.94
	6.85	6.92	6.80	0.74	1.8
% Mn	2.44	2.38	2.41	1.2	1.2
% Ni	9.65	9.92	9.68	0.31	2.5
	21.45	21.38	21.55	0.46	0.79
% Cr	15.75	16.15	15.81	0.39	2.1
	22.87	22.63	22.80	0.31	0.75
% Co	15.05	14.94	15.00	0.33	0.40
	6.35	6.19	6.30	0.79	1.7
% Fe	4.26	4.39	4.35	2.1	0.92
	17.20	17.10	17.25	0.29	0.87
	6.65	6.15	6.49	2.5	5.2
% Mo	15.92	15.56	15.85	0.44	1.8
	9.95	10.12	9.95	0.00	1.7
	3.65	3.48	3.62	0.83	3.9
% V	2.14	2.10	2.11	1.4	0.5
Average % Error				0.77	1.69

cal procedures, and are averages of several determinations.

Reproducibility of results depends upon the time allowed for an analysis, the element being measured, and its concentration. Each element responds to the primary x-radiation according to its atomic mass. The lower the atomic number, the longer the wave length. This is clearly discussed by Klug and Alexander,* C. S. Barrett;† or Cullity.‡ For instance beryllium (atomic number 4) has a characteristic wave length of 115.7 Angstroms (A) while molybdenum (atomic number 40) has a characteristic wave length of 0.71 A. The x-rays of interest for fluores-

* X-Ray Diffraction Procedures—Klug and Alexander

† Structure of Metals—Barrett

‡ Elementary X-Ray Diffraction—Cullity

X-RAY EMISSION SPECTROMETRY

cence analyses are in the range of 0.2 Å to 2.5 Å. Elements #12, Mg, to #22, Ti, have wave lengths larger than 2.4 Å. All the elements from atomic number 22, titanium, and up can be analyzed with the standard x-ray fluorescence equipment. Elements No. 12, magnesium, and up can be analyzed when helium gas equipment and a change of crystals are added to the standard equipment.*

All these elements can be measured by x-ray fluorescence from 1 percent to 100 percent, regardless of the other elements in the sample. Some elements such as iron, nickel and cobalt can be detected down to 0.001 % $\pm$ 10 % of the amount present.

When the elements are present in amounts above 10 percent, the system of taking counts versus time is accurate to ± 0.2 percent of the amount present. The accuracy is related to the amount of time allowed for an analysis. The above accuracy is for 102,400 total counts. If 10 percent chromium were analyzed for 3200 total counts, the result could be 9.88 percent to 10.12 percent. Taking 102,400 counts would change this to 9.98 percent to 10.02 percent.

For this reason the larger number of counts consistent with reasonably brief counting times should be used. In routine operation the counting time for 76,800 counts is two to four minutes. The accuracy is one percent or better of the nominal element concentration.

Nondestructive Technique. The samples for x-ray fluorescence can be liquids, powders, or solids. All wet chemical analyses on liquids require chemical treatment such as compound precipitation or qualitative separation. With the proper sample holder, liquids can be analyzed by x-ray and returned to their container unaffected. Powders can be compacted or simply poured into a sample holder and smoothed level. The powder method using compacts appears to be the most accurate, since it permits greater homogeneity of the sample as well

as the constant surface. Once a compact is formed, it can be placed in a storage file indefinitely after its use. Again, there is no harm done by the x-rays. Solid samples are the most common form subjected to x-ray fluorescence.

Nondestruction applies to the x-ray fluorescence standards as well. Once a standard sample is prepared, the only change made in the sample is an occasional refinishing on the polishing equipment. The amount removed from the surface of the standard is negligible. The standards are good for months or years, depending upon the production of the relative alloy. The only substances which show a visible change after x-ray irradiation are amorphous materials such as plastics and glass. One piece of clear plastic, after two years of use as a powder tray, visibly cracked on grain boundaries through its complete half-inch thickness. It then gradually erupted in small areas as a fine powder and had to be discarded. Glass will always take on a brown tint when struck by x-rays. This fact is used for centering the primary beam of the x-ray tube on the sample holder.

Sample and Standard Preparation. The sample required depends upon the test to be made. A qualitative analysis by x-ray fluorescence can be made on any solid or liquid as long as the elements are present in a measurable concentration, and the sample can be properly positioned in the equipment.

Quantitative analyses are more exacting. The sample should always be the same size. A convenient size specimen is a round disc $1\frac{1}{2}$ inches in diameter and about $\frac{3}{8}$ inch thick. The sample can be cast to this size or the proper thickness can be cut from a cast bar. Another sampling technique is to crush a metal sample or an ore sample to a powder of 325 mesh and finer, then to mix it and compact the powder to size.

Whatever the method of sample preparation used, the same must be done for the standard. Duplicate samples are recom-

* Norelco Report, Vol. IV No. I, Page 12

mended. One goes through x-ray analysis while the other is stored for reference by wet chemistry. Any solid sample used for x-ray quantitative analysis must have its surface processed for reproducible results. This means grinding on a 120 grit belt-grinder; milling; grinding on a high speed polishing wheel in a mill lathe, or even electropolishing, depending on the type of sample. The most common method is the first mentioned, but the surface requires a method of constant sample entry into the equipment. For reproducible results, put a reference notch in the back of the sample to aid repositioning in the sample holder. This requires a fiducial mark in the sample holder.

Lower Operating Costs. Analysis of an element by x-ray cuts the cost to less than $\frac{1}{2}$ that required by wet chemistry. The average wet chemistry analysis, which includes carbon determinations, is \$1.96. This includes labor, chemicals, equipment and the department's portion of the plant's overhead cost. The same analysis done by x-ray, after standards have been established, costs \$0.82. The latter cost does not take into account the fact that one sample was double-checked or another repolished and rechecked by x-ray. Actually, more analyses are made than are shown in the accounting.

Working Conditions. The atmosphere in which a person works often has a direct bearing on the quality of work. Temperature and humidity should be controlled for finite results with the x-ray goniometer. The temperature should be held to $\pm 3^{\circ}\text{F}$, and the humidity should be held to ± 5 percent when the normal is 50 percent. Fumes from dense smoke or acid cannot be tolerated. The x-ray tube housing and goniometer are brass and steel and hence easily corroded. Dust must be controlled to prevent sample contamination. The equipment and the operation demand clean, comfortably constant surroundings.

Analysis of Varied Physical Forms. The sample forms were briefly mentioned in

the paragraph on nondestructive testing. Liquid samples are normally of a low concentration, say less than 5 percent of the element to be analyzed. Therefore, a longer period of counting time, which will maintain the accuracy of the analysis, is required. Other than this, the details of analysis are exactly the same for liquids, powders and solids. The angle of measurement, the tube voltage, sample size, and the count intensity versus percent concentration curve calculations are the same. Homogeneity of the sample is no problem with liquids. Sediment in a liquid sample can either be centrifuged and decanted from the sample or continuously circulated in the sample holder. A pressed powder sample also behaves in a very homogeneous manner. The solid sample, however, is more of a problem. This will be discussed in the topic "Limitations".

The reproducibility of an analysis on liquids was tested by using a solution with two grams of nickel dissolved in nitric acid and diluted to 100 cc. The deviation in counting time was 0.2 second or $1\frac{1}{2}$ percent of the nominal concentration. This represents 0.03 gram of the 2 gram sample. This close a control can be matched by wet chemical methods but would require much more time and handling care.

A solid alloy sample with 2 percent nickel by weight was analyzed to see how it responded to x-rays compared to the liquid sample with the same quantity of the element. The sensitivity is much lower. A new set of standards and a new "counts per second versus concentration" curve have to be drawn. The reason for this is the depth of penetration of the x-ray beam in the sample. The density of the metal is cause for much greater absorption and limits the penetrability of the x-ray beam. A powder sample gives slightly higher counts per second than the solid metal sample. However, it still is not as responsive to the x-ray beam as the liquid sample. Therefore, a liquid free of particles and sediment is the most responsive

sample to x-rays and proportionally the most accurate due to the larger sample volume examined.

Equipment Modifications and the Basic Unit. A basic x-ray fluorescence unit comprises a power source and voltage regulator, an x-ray tube (usually a tungsten target), the beam collimating system, a crystal with a known lattice size, a detector and scaler-rate meter system, and a means of measuring the reflected angles. The reflected angle is measured precisely to the hundredth of a degree with a goniometer.

Many new electronic revisions of the latest equipment are available. Also, several sample compartment models and x-ray beam path systems have been developed since the first unit was sold commercially.

One major improvement of the x-ray spectrograph was the helium path equipment. The sample chamber, crystal holder, beam collimators and detector are bathed in helium gas to allow a beam path through an atmosphere less dense than air. This permits transmission rather than total absorption of the longer x-ray wave lengths. The latest development in this line is the vacuum spectrograph. The proper medium for the x-ray beam coupled with the best detector results in good resolution and intensity. Recently, one firm developed a modified collimator-detector system which reduced the intensity about 20 percent but increased the resolution over five times. This high-resolution modification requires reworking the present goniometer at the factory. The next improvement in efficiency is on the detector and signal amplification level. The first detectors used with x-ray spectrometry were Geiger-Muller tubes with either the argon-halogen or krypton gas fill. The efficiency of the detector depends upon the wave length of the element being analyzed. Maximum efficiency of the Geiger-Muller tube is restricted to a narrow range of wave lengths which cover the fourth period transition elements, roughly atomic numbers 24

to 35. New detectors have been developed which expand this range. The gas flow proportional counter has a maximum efficiency for atomic numbers 10 through 20. The proportional counter, which is a gas-filled side-window tube, has a maximum efficiency for atomic numbers 19 through 42. The scintillation counter covers the widest range of elements at maximum efficiency. It is sensitive to both hard and soft radiation for the elements with atomic numbers 22 through 100.

Two counters operating at maximum efficiency over the whole range can detect all the element wave lengths which can be measured by x-ray fluorescence. This fact has been put to use in the latest instrument developed for x-ray fluorescence. The flow proportional counter has windows on opposite sides of the detecting tube. Thus by mounting a scintillation counter on the same mounting arm, but just behind the proportional counter, the x-ray beam can be received by either detector.

The new vacuum spectrograph using this system of detectors will perform with near maximum sensitivity with a weak vacuum, approximately 1 mm of mercury. If a greater vacuum were obtained such as 1×10^{-6} or 1×10^{-7} mm of mercury, the efficiency of the unit would not increase much over 1 percent. One of the outstanding features of the vacuum unit is the crystal changing system. The change of crystals is performed by turning a lever, without touching the crystals or breaking the vacuum.

This feature is accomplished by redesigning the fluorescence unit. The tube tower, the rotating 4-place sample chamber, and crystal changer are built into one unit for easier vacuum control. It is the first production equipment which actually replaces part of the basic x-ray fluorescence unit rather than being appended to it.

Fluorescence Spectrometry Limitations

Element Range. The elements which are analyzed by the standard x-ray spectro-

graphic equipment are elements number 22 (titanium) through elements number 96 (curium). With the addition of helium path equipment (lighter-than-air path) it is possible to analyze elements down to atomic number 12, magnesium. This leaves the elements from 12 down, particularly boron and carbon, which cannot be analyzed by this method. The wave length of the element is the controlling factor for detection and analysis. At some future date we may see the proper combination of an energy source, diffracting crystal, and detector which will give an accurate quantitative analysis of all the elements.

Quantitative Limits and Precision.

Many elements can be analyzed by the x-ray spectrograph to levels as low as 0.001 percent or to the maximum of 100 percent. As higher energy x-ray source tubes are invented and detecting systems become more sensitive, the minimum limit of detection moves toward smaller decimal figures. Trace elements generally cannot be considered for fluorescence analyses. It is wiser to use the emission spectrograph and wet chemistry. In some cases, such as the analysis of aluminum in a high chromium alloy, the trace level is as high as 3 percent.

Vanadium with its low atomic number is seldom analyzed by fluorescence when the nominal content is below 0.5 percent. Iron, one of the fourth period transition metals, can be analyzed at levels of 0.001 percent and up. Again the wave length and absorption characteristics of the element dictate the level of analysis.

The quantitative limits at any percentage level are directly related to the quality of the standards. The standards must bracket the extreme limits of the pertinent elements. If more than four standards are made with less difference of the element between standards, and sufficient time is allowed for an analysis, it is possible to attain an accuracy which will surpass umpire wet chemical procedures. Standards for routine analysis

should cover a range of 5 to 30 percent for major elements and $\frac{1}{2}$ to 4 percent for minor elements. Normally, four standards are made for the production analyses of one alloy.

A study was made of potential equipment error using a sample with a nominal concentration of 10 percent nickel and leaving it in the machine for consecutive tests. This experiment using the constant sample gave a variation of twelve counts per second and a standard deviation of 4.8 counts per second, when only 25,600 counts were accumulated. This represents 0.22 percent nickel, and 0.08 percent nickel, respectively. If four times this number of counts are accumulated, the standard deviation drops to 1.6 counts per second, or 0.03 percent nickel. This increase in precision is a result of the statistical behavior of radiation detectors.

Size of Sample and Standard. The qualitative analysis of a sample does not demand uniform surface or uniform size. A two-degree-per-minute scan of the two theta angles usually constitutes the qualitative analysis. Only the relation of the wave length of the element and the indicating peaks at the detection angle are of importance. Quantitative analyses, on the other hand, are another picture. For precise quantitative results it is necessary to expose a constant area of the specimen in a consistent manner. A constant specimen size must be decided upon. For the program to be described, a convenient size specimen, $1\frac{1}{8}$ inches in diameter by about $\frac{3}{8}$ inch thick, was established as the standard. The specimen can be cast to size in an investment or sand mold, or it may be chill-cast in bar form and sliced to size. The latter is preferred for homogeneity. Usually it is necessary to design a holder to suit the chosen standard size of the sample. Any variation in positioning the specimen can lead to errors resulting from altering the geometry described in fundamental x-ray text books. Altering the position of the sample will affect the intensity of the diffracted rays. At the same time the area of the speci-

men exposed must be constant for each analysis, since this determines the total radiation incident on the analyzing crystal. Both of these requirements can be fulfilled by a rigid specimen holder that reproducibly positions and masks each specimen.

Cost of Standards. An enlightening example of standards cost appeared in a recent survey made on "Hastelloy" alloy 500. The alloy is composed of 13 elements. The cost of producing four reliable standards was approximately \$3,000.00. This covers raw materials, laboratory labor, x-ray labor and plant overhead. Laboratory labor plus plant overhead was over three-fourths of this cost. The bright side of the picture is the low cost of testing future samples, as discussed in the section on "Lower Operating Costs" p. 729.

To partially offset the initial cost of standards, it is possible to use one set of standards for several alloys in a series. It was shown that nickel in the 300 series stainless steels could be successfully analyzed using only one set of four standards. One working curve was produced for the whole family of 11 steels. The nickel content varies from 8 to 22 percent in this group. A similar circumstance exists with the cobalt-base alloys. Thirteen different alloy grades can be analyzed for tungsten from $3\frac{1}{2}$ to 18 percent with one set of standards for the whole group. Once again, it must be pointed out that these standards, for all practical purposes, are permanent.

Specimen Inhomogeneity and Diffraction Effects. The size and position of a sample have been discussed as to their relation to the x-ray beam. Other things which must be taken into consideration to gain reproducibility in the analysis of the sample are surface condition of the sample and surface condition of the standard. The method of surface finish depends upon the type of alloy to be analyzed. The corrosion-resistant and high-temperature alloys are finished on a 40-grit and 120-grit belt. The tool and wear-resistant alloys are now being finished on a

milling lathe. A high-speed alumina grinding wheel replaces the mill in the lathe. The sample and the standard must be refinished at the same time. Should the sample be polished on a belt other than the one the standard was polished on, the variation in condition of the belt is immediately detectable. Reproducibility checks on specimens finished on belts with 40-grit, 120, 220, 320, 400, 600-grit and 600-grit plus electrolytic etching were made on a "Hastelloy" alloy. The coarser finishes showed that a large error could be encountered when the grinding furrows were not always positioned in the same direction with respect to the x-ray path. This study also indicated that an orientation effect existed up to the 600-grit finish. However, it was determined that an excellent reproducibility could be obtained with the more convenient 120-grit finish when the grinding marks were consistently oriented. A small notch on the back of the sample serves as a reference.

Diffraction effects are possible in an x-ray spectrometer when the sample has a sufficient percentage of the element from which the target of the x-ray tube is made. For example, in certain positions such a sample radiated by a tungsten target beam will not only fluoresce, but also diffract the incident tungsten radiation in the direction of the analyzing crystal. The crystal, not being able to distinguish the two sources of radiation, will allow an excessive counting rate by the receiving tube. The orientation of the specimen is responsible for the error, since in most orientations the diffracted radiation will not reach the crystal. This problem was solved by designing and building a sample rotator. Since diffracted radiation is now incident upon the crystals so small a portion of the total time, the effect is diminished to the point of being an insignificant error. A sample rotator should be built to be asynchronous with the input x-ray machine current to eliminate the orientation effect.

Sample inhomogeneity can be a source of

analytical error. Tungsten is a notorious element for segregation in large-grained alloys or during slow cooling. The best means for eliminating the problem is to crush the sample and form a powder compact.

Initial Equipment Cost. With the prevailing prices, the initial cost of an x-ray spectrograph is roughly \$12,000. This price includes the x-ray transformer base and cabinet, the fluorescence target tube, the goniometer, the crystal, a detector, the rate meter and scaler, and a recording system. An average number of analyses made in a month in a production laboratory varies roughly from 600 to 1000 determinations. Using the figures (p. 729) which were \$0.82 for an x-ray analysis and \$1.96 for a wet chemistry analysis, a difference of \$1.14 per analysis can be seen. On this basis, a laboratory putting out 600 determinations per month could pay for this equipment in 18 months. A laboratory putting out 1000 determinations per month would pay for its equipment in 11 months. The initial cost of the equipment, therefore, should be viewed in terms of the work load of the laboratory.

Complex Electronic Controls. The first view of x-ray spectrographic equipment gives one the impression of a maze of buttons, dials, and switches. These controls are easily handled when broken down into three groups. One group is responsible for controlling the power to the x-ray tube. Another group controls the voltage of the detector system. The third group is responsible for amplifying and counting the signal which comes from the detector tube. The manual handling of the equipment can easily be learned in one week by a person of normal intelligence.

Repair of the manual x-ray equipment is usually limited to changing an electronic tube or a battery. Very seldom does more go wrong with the equipment. The doors of the power transformer are interlocked so that opening any door will shut off the equipment. Should the water pressure in the cool-

ing lines drop below minimum pressure, a pressure microswitch will shut off the equipment. A short in any part of the equipment past the transformer is detected and stopped by the safety overload relay on the transformer panel. Many safety devices are incorporated in the equipment. However, no machine is foolproof. Caution and care must be exercised in the handling of this electronic equipment.

Radiation Hazards. The x-ray spectrographic equipment is produced by the manufacturer to be free of any radiation hazards. The longer x-ray wave lengths known as the soft radiation are the wave lengths to be handled with great caution. These longer wave lengths are generally considered to be from 3 Å upward in length. Fortunately, the energy input into the x-ray tube is not sufficient to cause stray radiation 3 feet beyond the physical equipment, when the equipment is properly arranged. The stray radiation in this 3-foot limit seldom measures more than 25 milliroentgens. The causes for this can be improper equipment alignment, damage to the crystal surface, or improper beam collimation. If the equipment is used for technical service problems, it is sometimes necessary to modify the sample entrance opening. This makes it necessary to add additional shielding. There are many commercial means of detecting this stray radiation. The most common forms are pocket pen type dosimeters, film badge services which include wrist badges and pocket badges, rings with films as detectors, instruments which sit in the laboratory and collect total radiation over a period of time, and last, but finally, the simple method of a sheet of film in a cassette protected by black paper. Any method using film is at best a semiquantitative method of measurement. Special radiation detectors such as the Geiger counter or a scintillation counter are available to do on-the-spot checks of any stray radiation. The introduction of new sample compart-

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ments and automatic analytical equipment is eliminating the problem of stray radiation.

Industrial Applications. The x-ray fluorescence equipment was slow coming into the industrial market until World War II. Many colleges and universities had the equipment around 1930-1935. This could

have been a stimulus to the sudden growth in this field. There are currently over 2500 x-ray fluorescence units in operation in the United States. Lists of the companies using the equipment are available from the manufacturers.

The list in Table 2 is representative of the

TABLE 2. X-RAY FLUORESCENCE EQUIPMENT LABORATORIES

Ceramics	Televisions
Abrasives	Geology and Mineralogy
Glass manufacturing	(Mainly government offices other than firms dealing directly in Geology or Mineralogy)
Insulation	U. S. Department of Agriculture
Lava products	U.S. Department of Interior
Refractory materials	State government—Department of Roads and Irrigation
Chemistry	Medical
Ammunitions and powder	Coroners
Batteries	Dentistry
Cement	Hospitals
Cloth	Medical aids
Coke and coal products	Pharmaceuticals
Combustion products	Metallurgy
Dairy products	Aluminum products
Electric power plants (water and steam tests)	Arsenals (weapons)
Food manufacturers	Automobiles
Gas products	Bearings
Inks	Belt and chain products
Leather	Brass products
National Bureau of Standards	Business machines
Oil and petroleum products	Construction machines
Paint and enamel	Farm equipment
Paper products	Foundries
Photographic supplies	Gas turbines
Plastics	Gears
Police crime labs	Kitchen utensils
Radiation laboratories	Non-ferrous metals
Raw materials (manufacturers, e.g., boron and its compounds)	Piano parts
Rubber	Piston rings
Soaps	Pressure and temperature regulator parts
Synthetic fibres	Refrigerators
Tires	Screws and bolts
Tubing (rubber, metal and synthetics)	Steel and iron
Education	Stoves
Colleges	Miscellaneous
Universities	Aircraft
Research Institutes	Cork products
Rockets and Proving Grounds	Filter materials
Electronics	Historical museums
Electronic tubes and parts	Telephones
Electrical switches	U.S. Customs Department
Fuses	U.S. Navy, Bureau of Supplies and Accounts
Light bulbs	
Radios	

types of industries using x-ray fluorescence. The count per industry cannot be made, since records from the various companies have not been reported for the past year. As a good example for one industry, 250 units are used in the manufacture of quartz crystal oscillators. Examination of the lists used to compile Table 2 shows that 29 percent of the x-ray units are used in educational and research institutions.

Undoubtedly many specialty industries using x-ray fluorescence units have been omitted from the list. This is not intentional. At the same time, one group may apply under 3 or 4 major headings. The table does show the diversified use of x-ray fluorescence.

Example of One Alloy in Metallurgy

The use of the x-ray spectrograph for production chemical analyses has gained rapid recognition in industry. The instrument answers the three prerequisites of production analyses—accuracy, speed, and economy. Accuracy and speed have been touched upon in previous paragraphs. The economics of analyzing an alloy by x-ray is directly dependent on the quantity of production. "Hastelloy alloy C" will be used as an example of how an alloy is converted to x-ray analysis in the metallurgical industry. When an alloy is considered in great enough production to offset initial cost of standards, it is decided to convert the alloy from wet chemistry analyses to the x-ray method of analysis. It is then necessary to produce four standards, which are used to develop the working curves for the elements of this alloy. It is necessary to know the nominal composition of each element in the alloy and the limits of each. With this information, four heats bracketing these limits are produced. Satisfactory working curves were obtained for the nickel-base "Hastelloy C", when four elements were varied in concentrations simultaneously in four heats of the alloy. While the nickel content was held fairly

constant, 53.0 to 54.0 percent, chromium was varied from 14.0 to 16.0 percent, tungsten from 3.5 to 5.5 percent, iron from 4.5 to 8.0 percent, and molybdenum from 15.5 to 18.75 percent. Using this technique, only four standard samples were required to obtain four working curves. Varying one element each time would have required 24 sample heats. Wet chemical analyses have proved this short cut valid. Verification points may be added to the working curve by selection of routine samples of the same alloy for rigorous wet analysis. The technique of changing several element concentrations is safe, if the absorption characteristics of the matrix remain unaltered with respect to the primary x-ray radiation. This economical step toward obtaining standards will be applicable to many systems. For example, it was shown that nickel in the 300 series stainless steels could be analyzed using only one set of four standards.

Choosing the Elements to be Analyzed. The elements to be analyzed by x-ray fluorescence spectrometry do not include every element in the alloy. The x-ray spectrography is most favorably adapted to elements with a concentration of greater than 1 percent. Therefore, any trace element or the lower atomic number elements are usually analyzed in the wet chemistry laboratory or by emission spectrography. The matrix element of an alloy can be analyzed, but more often is considered the balance percentage of an alloy.

Program of Sample from Production to Result. The analysis of one or more elements of a production alloy is often required by x-ray spectrography while the heat is being held in the furnace. A sample is ladled into a mold and the alloy slugs are cast. The slugs are allowed about five minutes to cool and are then rushed to the laboratory for analysis. The samples are immediately polished (5 minutes), as is one standard, and then analyzed by x-ray fluorescence (5 to 15 minutes). The pouring

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time, sample preparation, and analysis take approximately 25 minutes. The results are promptly called back to the furnace room where corrections to the heat are made, if necessary. The introduction of automatic x-ray spectrographic equipment has cut the analysis time to less than half that required for the manual fluorescence unit.

Industrial How and Why of X-ray Fluorescence

A look at some of the uses within the industrial field explains how and why industry has accepted x-ray fluorescence so readily. The x-ray tube and equipment will operate continuously for thousands of hours. Continued operation is recommended, since the power control is regulated by electronic tubes. One particular tungsten tube has operated for over 20,000 hours, most of it continuous, but with input voltage continually varied to suit the concentration levels of the elements.

The equipment is easy to operate and maintain. The operator can generally perform the maintenance by replacing a battery or a tube to correct faulty operation. The large number of electronic tubes would appear to be a source of constant breakdown, but down-time normally is only one to two days a year. This involves a routine check of all tubes, oiling the recorder, cleaning the fluorescence housing, and greasing the high-voltage connection to the tungsten tube. The tubes are easily accessible and can be checked individually or in their operating sections.

A common use for the equipment would be quantitative analyses of elements (present above $\frac{1}{2}$ percent) in production samples. Another would be spot checks on unidentified samples. Raw material control, plant maintenance, safety hazards, scrap and reclaim, and surface inhomogeneities are a few of the uses for the equipment within one industry.

Special commercial modifications have been made in the field for continuous opera-

tion. These include petroleum flow-line units, uranium ore inspection lines, sheet metal and plating thickness control, and constant-level filling equipment for opaque wall containers. Another use would be effluent stream contamination control. It can be seen that the equipment is easily adapted to any type of sample, which again points up its versatility for industry.

REFERENCES

1. WEISERT, E. D. AND REITH, A. M., "The X-ray Spectrograph—A New Means of Rapid Chemical Analysis," Paper given at the 1956 Denver Research Institute X-ray Conference.
2. "Norelco Reporter," Volumes I through VI, Philips Electronics, Inc., Mount Vernon, New York.
3. "G. E. Radiation Digest," General Electric Company, Milwaukee 1, Wisconsin, X-ray Department.
4. "X-ray Diffraction and Geiger Counter X-ray Spectrometric Equipment," North American Philips Company, Inc., Mount Vernon, New York.
5. CULLITY, B. D., "Elements of X-ray Diffraction," Addison-Wesley Publishing Company, Reading, Massachusetts.
6. BARRETT, C. S., "Structure of Metals," McGraw-Hill Book Company, New York.
7. KLUG, H. P. AND ALEXANDER, L. E., "X-ray Diffraction Procedures," John Wiley & Sons, Inc., New York.

W. J. WITTIG

COMPLEX SYSTEMS: INTERELEMENT EFFECTS

The fluorescent line spectra produced by x-rays are comparatively simple, and in complex mixtures one or more lines characteristic of each element present are usually free from interference. Quantitative analysis is made possible by the proportionality of fluorescent intensities to concentration. However, the recorded intensity of the spectra emitted from a sample depends on instrumental design and operating conditions as well as the sample composition. Intensities vary with the optical system (including type of collimation and detection), excitation

conditions (including the x-ray tube design, its operating potential and current), sample area, thickness and grain size. Assuming controlled conditions of the instrument and the sample, the line intensity of an element will vary with total sample composition, as well as that element's concentration, due to the absorption effects which are commonly designated as "interelement effects." These effects may be predicted qualitatively; they may be corrected using one of a variety of techniques for sample preparation and intensity-composition correlations.

Absorption Effects

Beattie and Brissey² state that if it were not for these absorption effects, the intensity of the fluorescent radiation from an element in an alloy would be proportional to the atomic density of that element and a quantitative analysis could be made from the ratio of intensity in the alloy to the pure element; absorption effects arise because the incident x-rays penetrate a significant distance below the specimen surface. A sample which is infinitely thick (i.e., absorbs all the exciting radiation) will exhibit the maximum disturbing effects; for an infinitesimally thin sample the absorption effects would be at a minimum.³

The absorption involves a number of considerations. Among these Sherman¹⁴ describes the absorption of the beam by the specimen, the sharing of which will be governed by sample composition, and the absorption by the sample of the fluorescent radiation itself, varying with sample density and matrix.

The magnitude of an absorption is given in terms of the "absorption coefficient" and has been considered in detail by many workers^{5, 6, 16} since Barkla and his associates first studied the process of absorption. X-rays are more strongly absorbed by some substances than by others. The "mass absorption coefficient" gives the fraction of the energy which is absorbed when a beam of

unit cross section traverses a unit mass of material. It is characteristic of the absorbing material, but independent of its physical state. The mass absorption coefficient of a combination of elements (e.g., a compound or alloy) is the sum of the mass absorption coefficients of all the elements (for the wavelength in question) in proportion to their composition by weight.^{3, 6} Extensive absorption coefficient data have been accumulated, and tables of these values have been published.⁶

If the mass absorption coefficient of an element is plotted as a function of wavelength, a striking discontinuity or drop appears at a wavelength which is critical for that element. These discontinuities or "absorption edges" are characteristic of each of the chemical elements and represent the minimum energy necessary for their excitation. All x-rays of shorter wavelength than the edge will be absorbed by that element to a considerably greater extent than wavelengths just longer than this critical value. A single edge is associated with the K series, 3 with the L series, and 5 with the M series lines.

Mathematical Treatment

Formulas relating fluorescent x-ray intensities to chemical composition have been developed by Beattie and Brissey,² Gillam and Heal,⁸ Sherman,^{14, 15} and Noakes,¹³ among others. Gillam and Heal have shown that if mutual fluorescence is neglected, the intensity of a fluorescence line in a binary homogeneous mixture is related to the concentration of the two elements and to their mass absorption coefficients for the incident and for the fluorescent radiation. The intensity is given by:

$$I_a = \frac{K_a}{a(\mu_1 + \mu_2)_a + b(\mu_1 + \mu_2)_b}$$

where

I_a = measured intensity of element a

K = proportionality constant

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- a, b = concentration of elements a and b
 μ_1 = mass absorption coefficient for the incident radiation
 μ_2 = mass absorption coefficient for the fluorescent radiation

Using statistical considerations, Sherman extended correlation theory to include multi-component mixtures. Assuming a monochromatic incident beam of wavelength shorter than the fluorescent radiation from the element, he first¹⁴ developed the intensity-composition relationship for the element of highest atomic number in a 2 or 3 component system. The intensity of the elements of lower atomic number is complicated by "mutual excitation" effects due to the fact that the characteristic spectra of higher atomic number elements are sufficiently energetic to excite their spectra. The relations also become more involved if the incident beam is polychromatic; Sherman describes the analytical curves as hyperbolas in space, the dimensions of which depend on the components in the mixture. He presents an empirical linear approximation which may be used for limited ranges of composition. Sherman¹⁵ further amplified the theoretical derivation of intensities using statistical and graphical methods.

Noakes¹⁸ developed an absolute method of analysis of 2 and 3 element systems which he applied to stainless steels. Intensity relationships are based on instrumental optics as well as linear absorption coefficients and sample composition. Coefficients of absorption and enhancement which were determined experimentally for iron, nickel, and chromium may be used for stainless steel analyses in other laboratories.

In spite of the progress which has been made in the theory of the correlation of concentration with intensity, its application is an extremely complicated chore. Also, in order to obtain agreement between experimental and theoretical values many assumptions must be made which do not necessarily

hold in practice. However, empirical relations have been developed which are useful.

Beattie and Brissey² obtained accurate analyses of 3 and 4 element combinations by substituting empirical absorption parameters relating the intensities of pairs of elements to their weight percentage, into simultaneous, linear equations. These parameters are defined as follows:

$$A_{ab} = \frac{W_a}{W_b} (R_b - 1)$$

$$A_{ba} = \frac{W_b}{W_a} (R_a - 1)$$

where

A_{ab} = the absorption parameter of element b for element a

A_{ba} = the absorption parameter of element a for element b

W_a = the fractional weight of element a in the alloy standard

W_b = the fractional weight of element b in the alloy standard

$R_a = I_{aa}/I_{as}$

I_{aa} = intensity from a pure element specimen of a

I_{as} = intensity from the alloy standard etc.

Mitchell^{11, 12} used empirical arithmetic corrections for the analysis of systems of up to 6 components. In a system of elements A, B, C, D, E, and F, the intensity of element A is corrected for the presence of C, D, E, plus F, and analyzed as if there were only a two-component system of A and B. Absorption or enhancement corrections are based on the measured intensities of 3-component standards containing varying percentages of A, B, and the interfering element. The "correction factor" is the ratio of the intensity of A in a matrix of elements B and C to its intensity in matrix B. A formula for the adjusted intensity of A in matrix B follows:

$$I_{AB} = I_0(F_{ACB} + F_{ADB} + F_{AEB} + F_{AFB})$$

where

I_0 = the observed intensity
 F_{ACB} = factor for effect of C on A in B
 etc.

Prediction of Interelement Effects

Quantitative analysis of a sample by x-ray spectrography is facilitated by prior qualitative examination for its major constituents. Knowledge of the sample matrix allows general prediction of the absorption effects which will occur. Intelligent selection of the appropriate method for interelement effect correction and choice of analytical lines subject to a minimum absorption are then possible. Interelement effects can be predicted by a study of mass absorption coefficients and the relative positions of x-ray lines and element absorption edges. Tabulations of absorption edge and emission line wavelengths are readily available.^{4, 6, 17, 18}

General and Specific Absorptions. The effects fall into two categories (1) general absorption of the element fluorescent radiation by the matrix, and (2) specific absorption or enhancement of the radiation by the matrix.

(1) The mass absorption coefficient of a given material for a given radiation (or of a given radiation by a given material) characterizes both the material and the radiation. The coefficient for a given material decreases with decreased wavelength of the radiation (except at absorption edges); the coefficient for a given wavelength increases with increased atomic number of the given material. Consequently, a light element emitting long wavelength radiation in a heavy element matrix is strongly absorbed and its intensity is low at low concentrations; e.g., titanium ($Z = 22$) in a tantalum ($Z = 73$) matrix. Generally, the absorption of the radiation from a heavy element by a light matrix is small, and its intensity is high at low concentrations; e.g., uranium ($Z = 92$) in iron ($Z = 26$). Refer to Figure 1 for

typical calibration curves. However, since the L series radiation of an element is softer (longer) than its K series radiation, the L series of heavy elements such as the rare earths ($Z = 57$ through 71) will be more highly absorbed than the K series by light elements such as titanium or calcium ($Z = 20$). Generally, the degree of absorption of an element by its matrix will depend on the interrelation of the mass absorption coefficients of the matrix elements for that element.

(2) Category (2) is an extension of (1) in which the interelement effect is a more specific absorption-enhancement which occurs due to the proximity of absorption edges and emission lines. Since the mass absorption coefficient of an element increases with the wavelength of the absorbed radiation until an absorption edge is reached, drops at this point and then increases again with wavelength, radiation shorter than the absorption edge will be absorbed to a greater extent than radiation just on the long side of the absorption edge. The absorption of radiation shorter than the absorption edge of an element results in the excitation or enhancement of the fluorescent radiation of that element.

Effects Occurring in K Series Spectra. In the case of the K series of elements adjacent to one another in the periodic table

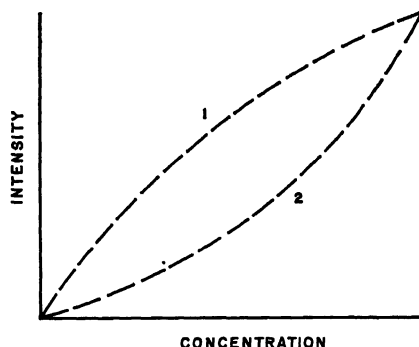


FIG. 1. Typical intensity vs. concentration calibration curves; Curve 1 represents a heavy element in a light matrix; Curve 2 represents a light element in a heavy matrix.

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from atomic number 22 through the rare earth series, only moderate effects occur, and intensities of the K alpha lines are nearly linearly related to concentrations; for example, Cb K alpha or Zr K alpha in a columbium-zirconium ($Z = 41$ and 40) system; Fe K alpha or Mn K alpha in an iron-manganese ($Z = 26$ and 25) system (refer to Figure 2). However, in the case of some adjacent elements in this group, it may not be possible instrumentally to resolve the K alpha line of the higher from the K beta of the

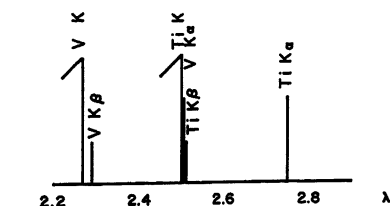
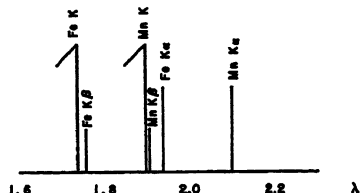


FIG. 3. Examples of K series emission line-absorption edge relationships for 2 and 3 element combinations.

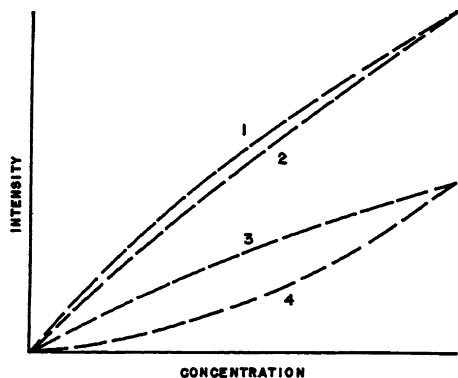


FIG. 2. Typical emission line-absorption edge relationships and calibration curves for the K series of adjacent elements from atomic number 22 through the rare earth series; Curves 1 and 3, respectively, represent the K alpha and K beta line intensities of the lower number element; Curves 2 and 4, the K alpha and K beta line intensities of the higher number element.

the lower atomic number element; for example, V K alpha at 2.50 Å and Ti K beta at 2.51 Å. Then it becomes necessary to use the K beta of the higher number element (V K beta in this case) as its analytical line, in which case a severe absorption is exhibited due to its location on the short wavelength side of the absorption edge of the lighter element (Figure 3). In fact, the K beta line of the heavier of any 2 or more adjacent element combinations suffers absorption by the lighter elements, being most severely effected by the element immediately adjacent. If, as in Figure 2, the Fe K beta or Cb K beta were chosen as the analytical lines, they would exhibit absorption by manganese or zirconium, respectively. The Fe K beta line in a combination of iron, manganese, and chromium ($Z = 26$, 25 , and 24) would be absorbed by both manganese and chromium; Mo K beta in a combination of molybdenum-columbium-zirconium ($Z = 42$, 41 , and 40) would be absorbed by both columbium and zirconium (Figure 3). The lighter elements are enhanced as a result, but generally only to a small degree.^{3, 13} Where there is an interference on the K alpha (first order) line of

an element in a multi-component mixture and the K beta line is severely absorbed, use of the K alpha (second order) line may be advantageous. In the molybdenum example cited, the peak-less-background intensity of the Mo K alpha (second order) line using a NaCl crystal is significantly higher than the peak-less-background intensity of the Mo K beta.

In combinations of three adjacent elements from Atomic No. 22 to 35, no general pattern appears and variations in effects occur. There is a gradual shift through this group of the K alpha lines of the two higher elements, so that by Atomic No. 35, all the K alpha lines of a three-element combination are on the high side of the absorption edges, thus freeing them from specific absorption. A major problem in the first few elements from No. 22 up is line interferences on both K series lines of the middle of three elements. The V K alpha line has a Ti K beta interference and the V K beta line has a Cr K alpha interference. On most instruments these are not resolvable or separable by PHA. The situation for chromium-manganese-iron is somewhat less severe and on many instruments either manganese line may be usable. In this case the Mn K alpha is preferable because of its sensitivity and location on the high side of the three edges. Combinations of three elements from No. 35 to the rare earths are typified by zirconium-columbium-molybdenum and lanthanum-cerium-praseodymium. The K alpha lines of each of the three elements are on the high side of the edges. However, the higher element in each case is subject to some line interference from the K beta of the lower element, e.g., the Mo K alpha and Zr K beta which are 0.008 Å apart, and the Pr K alpha and La K beta which are 0.016 Å apart. In addition, even if sufficient kilovoltage is available to excite the K series of heavier elements such as the rare earths, fine resolution is necessary to separate the K alpha lines, there being less than 0.015 Å dif-

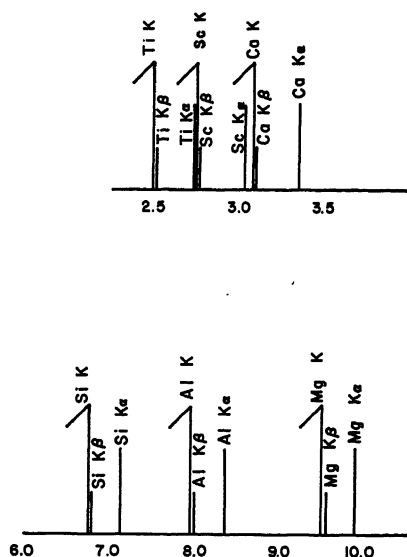


FIG. 4. Typical K series emission line-absorption edge relationships for elements from atomic number 12 through 22.

ference between the Ce K alpha and the Pr K alpha or the Ce K alpha and the La K alpha. If sufficient resolution is available, the K alpha lines in such combinations are preferable.

The relative positions of the absorption edges and emission lines of adjacent elements less than $Z = 22$ are shown in Figure 4 for calcium-scandium-titanium and magnesium-aluminum-silicon combinations. This region from $Z = 12$ through 22 offers the simplest x-ray spectrum and combination of 2 or more elements are free from line interferences (except for several second order lines). In combinations of 2, 3, or more adjacent elements, both K series lines of the heavier element are absorbed by the lighter elements, the effect being severest with titanium-scandium and least with aluminum-magnesium.

Effects Occurring in L Series Spectra. Because of excitation requirements, elements of the rare earth series and higher atomic number are analyzed by measurement of their L series spectra. The multiplicity of L series lines and L absorption edges causes

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their relationship to be somewhat more complex than K series lines and edges, and prediction more difficult. Figures 5 and 6 illustrate this relationship for combinations of rare earth elements from lanthanum ($Z =$

57) through samarium ($Z = 62$) and for tantalum-tungsten combinations ($Z = 73$ and 74). The choice of lines will be determined by the interferences occurring in complex matrices. In a lanthanum-cerium-

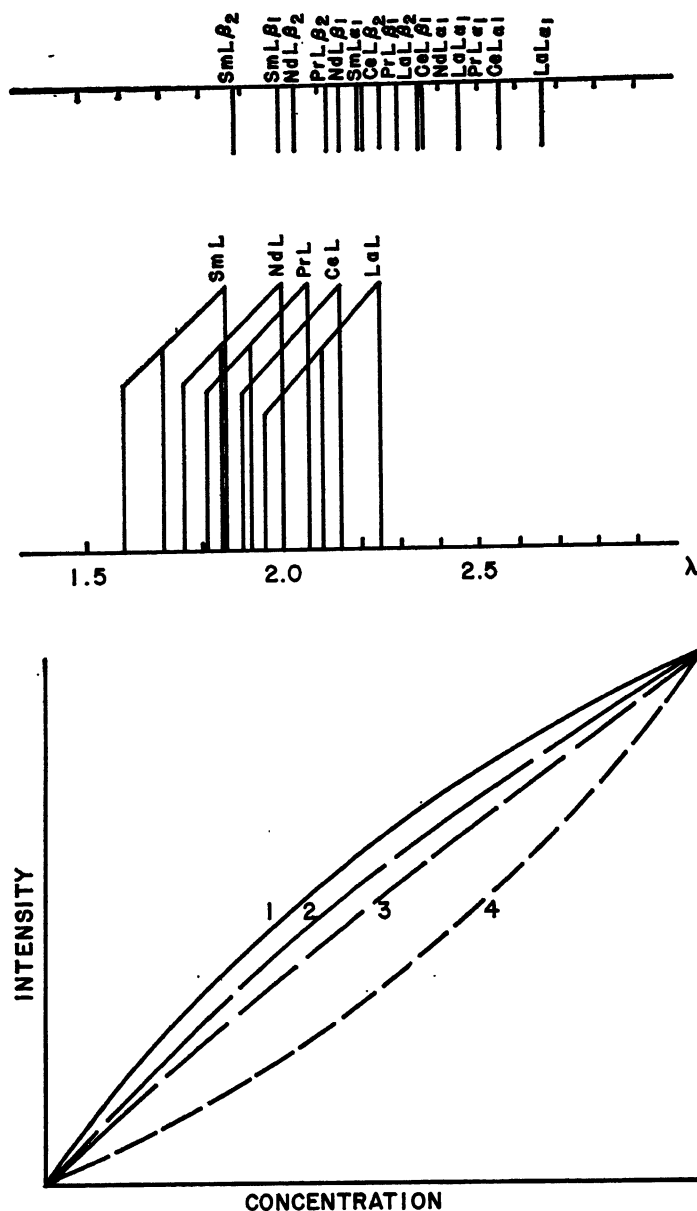


FIG. 5. Emission line-absorption edge relationships and a typical calibration curve family for the L series of rare earth elements from lanthanum through samarium; Curves 1, 2, 3, and 4 represent the K beta 1 line intensity of praseodymium in cerium, neodymium, samarium, and lanthanum.

praseodymium-neodymium-samarium mixture, the intensity of lanthanum L alpha varies generally with matrix, since it is absorbed less by cerium than by praseodymium, neodymium, or samarium in that order. It is almost linearly related to concentration, being on the high side of the L absorption edges of each of the group, and being subject to general absorption by the matrix as well as enhancement by its characteristic radiation. The intensity of Ce L alpha is similarly almost directly proportional to its concentration and varies generally with matrix, being absorbed less by lanthanum than by praseodymium, neodymium, or samarium. The choice of the L beta 1 lines of praseodymium, neodymium, and samarium is usually necessary due to fairly close interferences on their L alpha lines. Nd L beta 1, being on the short wavelength side of the La L III absorption edge, is specifically absorbed by that element and generally absorbed by cerium, praseodymium, and samarium. Pr L beta 1 at 2.26 A, virtually the same wavelength as the L III absorption edge of lanthanum, is absorbed by that element. Sm L beta 1 at 2.00 A is subject to some absorption by lanthanum and praseodymium (L II at 2.10 A and L III at 2.08 A, respectively) and slight absorption by cerium (L III at 2.16 A). These effects due to the interrelationship of lines and edges are typical examples of L series spectra. The L alpha 1 lines of adjacent elements are subject to general absorption; some enhancement of the L spectra of the lighter element may occur due to "mutual enhancement" effects. If combinations of more than 2 adjacent elements are to be determined, line interferences may necessitate the choice of analytical lines subject to specific absorption effects.

Internal Standard Considerations. In the use of internal standards for quantitative spectroscopy, knowledge of interelement effects is essential; the subject has been thoroughly covered by Von Hevesey,¹⁰

Glocker and Schreiber,⁹ and Adler and Axelrod.¹ The critical factors in the choice of an internal standard for an element adjacent to it in the periodic table may be summarized as follows:

Absorption Effects. (a) The change in intensity ratio due to the preferential absorption of the longer wavelength line by a third element having an absorption edge on the long wavelength side of the two lines being measured.

Although Von Hevesey calculated and observed examples of small effects in intensity ratios, Adler and Axelrod found that even when the comparison elements, e.g., columbium-molybdenum or chromium-manganese are severely absorbed by the third element, their ratio is fairly constant.

(b) The change in intensity ratio due to the presence of an element with an absorption edge between the two lines being measured.

The magnitude of absorption of the shorter radiation obviously is large. To avoid a disturbing absorption effect, Von Hevesey recommends choosing comparison lines as close together as possible, the lower limit of their proximity being fixed only by the instrumental ability to distinguish between them.

Excitation Effects. (a) The presence of a line of a third element between absorption edges of the two elements to be compared.

Von Hevesey indicates that a disturbing effect occurs only when the line of the third

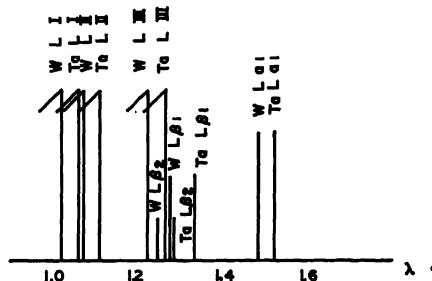


FIG. 6. Example of one type of L series pattern for adjacent elements.

element is an intense one. Its radiation can excite the softer edge, but not the harder one, and the intensity ratio will be changed in favor of the line having the softer edge. Adler and Axelrod describe typical cases where this relative enhancement is large.

(b) The presence of a line of a third element on the short wavelength side, but much closer to the edge of one of the two elements to be compared. The intensity ratio in this case may be affected because of differences in the excitation of the 2 lines being compared. However, the enhancement effect is fairly small, even when the edges are widely separated and the exciting line is strong.

Von Hevesey also points out other disturbing effects which may occur such as mixed excitation of characteristic lines because of enhancement by the x-ray tube target spectrum.

Simplifications. In the prediction of the interelement effects occurring in complex combinations, many simplifications may be made. Because of the fixed pattern of x-ray wavelength and absorption edge with atomic number, elements adjacent to one another in the periodic table are affected by and affect certain other elements in a similar manner. For example, Cb K series lines are specifically absorbed by tantalum to about the same degree as by tungsten or hafnium, and are generally absorbed by titanium to about the same degree as by vanadium. Zr K series lines are selectively absorbed by tantalum, tungsten, or hafnium and generally absorbed by titanium and vanadium to almost the same degree as is columbium. This similarity in absorption behavior, of course, is the basis for internal standardization. It also permits short-cutting the standardization for complex combinations by reducing the number of standards or corrections necessary.

Progress in Interelement Effect Correction

Increased awareness of the basic principles involved in x-ray absorption and of the

pattern correlating x-ray fluorescent intensities with composition will make possible more extended and more accurate use of x-ray spectrography as an analytical tool.

Improved instrumental optics (particularly in resolution and in extension to the very short wavelength region) and increased available power for sample excitation will make possible the choice of analytical lines subject to a minimum of absorption effects.

Quantitative tabulations of absorption effects in multi-component systems will be published. Data processing and computing equipment will be programmed using these quantitative absorption-enhancement values for line intensity correction and for true direct reading of compositions.

REFERENCES

1. ADLER, I., AND AXELROD, J. M., *Spectrochim. Acta*, **7**, 91 (1955).
2. BEATTIE, H. J., AND BRISSEY, R. M., *Anal. Chem.*, **26**, 980 (1954).
3. BRISSEY, R. M., LIEBHAFSKY, H. A., AND PFEIFFER, H. G., ASTM Spec. Tech. Publ. No. 157, 43 (1954).
4. CAUCHOIS, Y., AND HULUBEI, H., "Tables de Constantes et Donnees Numeriques. I. Longueurs D'Onde des Emissions X et des Discontinuites D'Absorption X (Hermann, Paris, 1947).
5. CLARK, GEORGE L., "Applied X-rays" 4th Ed., New York, McGraw-Hill Book Co., 1955.
6. COMPTON, A. H., AND ALLISON, S. K., "X-rays in Theory and Experiment," New York, D. van Nostrand Co., 1935.
7. COPE, J. H., *Norelco Reporter*, **3** (March-September 1956).
8. GILLAM, E., AND HEAL, H. T., *Brit. J. Appl. Phys.*, **3**, 353 (1952).
9. GLOCKER, R., AND SCHREIBER, H., *Am. Physik*, **85**, 1089 (1928).
10. HEVESY, G. VON, "Chemical Analysis by X-rays and Its Applications," New York, McGraw-Hill Book Co., 1932.
11. MITCHELL, B. J., *Anal. Chem.*, **30**, 1894 (1958).
12. MITCHELL, B. J., Tenth Annual Symposium on Spectroscopy, Chicago, Illinois (June 1959).
13. NOAKES, GORDON E., ASTM Spec. Tech. Publ. No. 157, 57 (1954).
14. SHERMAN, J., ASTM Spec. Tech. Publ. No. 157, 27 (1954).

15. SHERMAN, J., *Spectrochim. Acta*, 7, 283 (1955).
16. SIEGBAHN, M., "The Spectroscopy of X-rays," London, Oxford University Press, 1925.
17. ZINGARO, P. W., *Norelco Reporter*, 1 (March-April 1954).
18. ZINGARO, P. W., *Norelco Reporter*, 1 (May-June 1954).

BETTY J. MITCHELL

ELECTRON PROBE MICROANALYZER

One of the very newest contributions to x-ray spectroscopic techniques is the successful design and commercial production of the so-called electron probe, or point-by-point microanalyzer. This was first developed by Castaing³ in France in 1951. Its purpose is to provide a means of excitation of primary x-rays in individual grains or particles in powders or aggregates as small as a micron in diameter, so that variations in chemical composition may be traced in passing from one grain to another. The probe is unique in several respects and comprises the following features:

(1) The electron beam, used for bombarding the target (a single grain) in analogy with a conventional x-ray tube, is collimated into a fine pencil of $1\ \mu$ or smaller cross section by means of magnetic lenses exactly as in the electron microscope. This beam thus excites x-rays essentially from a point source.

(2) The specimen may be moved by a translation mechanism so that any desired area may be brought into position for analysis.

(3) An optical microscope system is built into the instrument for direct observation of the area undergoing analysis.

(4) The spectrometer for analysis of the emitted characteristic x-radiation is specially designed to make best use of the very small beam, and usually depends upon focusing curved-crystal optics.¹

It should be noted that this technique is currently the only one using the original primary x-ray beam spectrometry in which the specimen is pasted on a target and bombarded with electrons from the cathode. The

present powerful secondary fluorescent x-ray spectrometry (q.v.) used almost exclusively for analysis is not adapted for the microprobe analyzer for two reasons: (1) it is almost impossible to collimate a primary x-ray beam down to a micron or less in comparison with the magnetic lens control of an electron beam; (2) the total intensity of the secondary fluorescent beam from 1-micron areas is too low for quantitative measuring. The intensity of the primary x-ray beam is 200 to 1000 times greater than that produced by the same sample by fluorescence. Thus at least 0.1 % of an element is generally detectable.

The designs and operation of electron guns, electromagnetic lenses and apertures, and corrections for astigmatism and spherical aberration of these lenses are generally well known from electron microscope development, and for microprobe purposes are discussed in detail by Birks in his book.¹ The specimen chamber, which of course must be operated at a Coolidge vacuum characteristic for any x-ray tube with hot filament cathode, is a precision instrument with a translation mechanism capable of positioning the specimen to within 1 micron of the exact area required and scanning successive areas along a line. X-rays pass through a beryllium or "Mylar" window into the crystal spectrometer which itself must be evacuated for analysis of the lighter elements. In a design by Duncomb⁵ the electron beam is swept back and forth over a $\frac{1}{2}\text{ mm} \times \frac{1}{2}\text{ mm}$ area of the specimen surface; the x-ray output of the scanning may be displayed on a television-type tube synchronized with the scanning of the specimen.

The spectrometer employing¹ curved crystal optics to make maximum use of the 1-micron focal spot may be used to scan the whole spectrum or, with multiple fixed crystals and detectors, as discussed under x-ray emission spectroscopy, may be used to record intensities of several elements simultaneously and continuously as the specimen is translated. The choice of crystal analyzer, discussed on page 751, is dictated by wave

length ranges and resolution required. LiF crystals are generally convenient as in fluorescent x-ray spectroscopy. Detectors are also Geiger, proportional and scintillation counters, with the same electronic circuits; and nondispersive (filter) systems may also be used as in the fluorescent spectral analyses.

Not all specimens suitable for fluorescent analysis can be adapted for successful examination by the electron probe. Liquids volatilize on the high vacuum; some specimens are unstable in the intense electron beam, as is also true in electron microscope; the surface must be smooth to avoid variations in x-ray output; and the specimen must be electrically conducting, or made so by deposition of a thin metallic layer. Absorption effects in quantitative interpretations are much smaller because of surface excitation and path length for x-rays of only a few microns: but enhancement of line intensities (for example excitation of Ti $K\alpha$ by Fe $K\alpha$ in an alloy) may introduce errors, which may be corrected by means of standard samples of known composition containing the same elements.

Though this technique is still very new, several interesting applications have been reported, involving analysis *in situ* of segregations or precipitates in metals, such as carbides in iron matrix, and variations in composition in one particular carbide to another (impossible by chemical analysis). Intermetallic diffusion was one of the first problems studied by Castaing.⁴ The probe detects how sharp phase boundaries are or, where there is a continuous range of solid solutions, the extent of diffusion as a function of time and temperature, and hence the diffusion coefficient as in the Ti-Zr system; or the greater speed of diffusion along grain-boundaries as in the Zn-Ag alloys. A very useful analysis is that of depletion of one or more elements in a matrix near a surface undergoing oxidation or corrosion, as in 18-8

stainless steel for which Cr is depleted for 10 microns below the surface.

Mineralogists and geologists are very much intrigued by the possibilities of the electron probe, not only in analysis of segregation, but also in trends in composition of minerals bedded in specific directions. Typical of these possibilities is the analysis of minute inclusions (0.03 mm) in a copper-iron mineral (2). These grains were found to contain 55 % Fe and less than 5 % Cu and corresponded to FeS; hence the mineral previously called vallerite in high temperature copper ores is distinct from a Swedish type.

Biological problems are now being solved with the electron probe. For example Birks¹ described the analysis of bone for calcium content in going from bone (30 %) to cartilage (0 %), occurring chiefly in the region between bone cells. The test of uniformity of staining of biological specimens with OsO_4 or phosphotungstic acid prior to electron microscopic examination of cell structure is another useful service.

In the words of Birks, who has had an important role in developing the electron probe at the Naval Research Laboratory, "it appears to have a great future because there are few techniques that can detect of the order of 10^{-13} to 10^{-14} gram of an element, or can perform chemical analyses on areas as small as 1 micron." This new probe has served further to generate interest and effort in the design of a multiple-type instrument utilizing the basic electron gun-magnetic lens system with proper rearrangement of other parts for (1) electron microscopy; (2) electron diffraction; (3) electron probe microanalyzer; (4) projection x-ray microscope; (5) micro fluorescent x-ray spectral analyses; (6) micro x-ray diffraction. Commercial apparatus already provides some of these choices with the same basic unit.

REFERENCES

1. Birks, L. S., "X-ray Spectrochemical Analysis," Interscience Publishers, N.Y., pp. 137 (1960).

2. BIRKS, L. S., BRODES, E. J., ADLER, I., MILTON, CHARLES, *Am. Mineralogist*, **44**, 974 (1959).
3. CASTAING, R., Thesis, University of Paris (1951).
4. CASTAING, R., AND GUINIER, A., *Anal. Chem.*, **25**, 724 (1953).
5. COSSLETT, V. E., AND DUNCUMB, P., "Electron Microscopy," Proc. Stockholm Conf., Academic Press, N.Y., p. 12 (1956).

Cross references: *Electron Microscopy, Fundamentals of X-ray Emission Spectroscopy*

G. L. CLARK

FUNDAMENTALS

Development of X-Ray Emission Spectroscopy

Röntgen, who discovered x-rays on November 8, 1895, in his experiments with cathode rays, made every effort to produce a spectrum of a beam of x-rays, assuming that these invisible rays belonged in the same electromagnetic spectrum with visible light, ultraviolet, infrared, and Hertzian or radio waves. His logical experiments designed to disperse a beam by refraction by prisms and diffraction by ruled gratings were unsuccessful because of failure to recognize that the refractive index was less than 1 by a quantity of the order of 0.000001 and that diffraction by the grating required that the beam have an exceedingly small grazing angle of incidence. Thus from 1895 to 1912 there was no method of x-ray spectrometry and the nature of x-radiation remained mysterious. By absorption measurements of x-ray beams, Barkla in 1905 found evidences of discontinuities in such properties, as if under proper conditions of excitation the energy of emission was distributed in groups instead of continuously. As a matter of fact he devised the nomenclature used to this day, namely, K, L, M, N, O, P series by analogy with series in the optical spectrum of hydrogen. But, of course, these absorption measurements did not permit resolution of characteristic spectral emission lines or absorption edges. It was the experiment

in 1912 by von Laue and his associates, Friedrich and Knipping, proving that all crystals are three-dimensional diffraction gratings for x-rays, and the subsequent derivation of the Bragg law, $n\lambda = 2d \sin \theta$ [where n is an integer, the order of the spectrum; λ is the wave length of a ray reflected (or diffracted) by a set of planes in a crystal of spacing d , at an angle of incidence, θ], which opened the way for the construction of a crystal spectrometer.

It was put to use by the Braggs, Moseley, Siegbahn, and many others, to resolve x-ray beams into spectra with emission lines characteristic of the chemical element serving as the target in the x-ray tube. Of course the von Laue experiment proved the electromagnetic nature of x-rays, even though it was not until after 1920 that refraction by prisms and diffraction by ruled gratings were successfully proved. The Bragg ionization spectrometer consisted of a central movable table upon which the crystal analyzer could be rotated to vary the angle of incidence θ read on a scale, and an ionization chamber which could be mounted on a rotating arm, the position of which could also be read on a scale. It was soon clearly understood that when a target was bombarded by a stream of electrons in an evacuated bulb, the electrons were stopped by the target atoms and their kinetic energy transformed, by a process involving the inner electrons in the atoms, into x-radiation.

Further, it was apparent that at all voltages on the x-ray tube x-rays were generated which had a continuous, or "white," spectrum, independent of the atomic number of the target but that above certain critical voltages radiation was generated which gave sharp lines (or peaks on the spectra plotted from spectrometer readings), in series already designated by Barkla, with the letters K (for groups of four principal lines with the shortest wave lengths generated at the highest critical voltage), L, the next longer group of about 20 lines, and the still longer M, N,

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O, and P series. These were emission lines and series, characteristic of the chemical elements in the continuous progression of atomic numbers whose significance for the first time was proved by Moseley with a Bragg spectrometer. So began the accurate measurement of the wave lengths of these x-ray lines (and associated characteristic absorption edges) as a means of spectrometric identification of any unknown sample thereafter which could be pasted on a target and bombarded with electrons in the x-ray tube.¹⁶ The values of these characteristic wave lengths of K and L series lines for almost all the chemical elements are tabulated in readily available handbooks.

There were immediate advantages of x-ray in comparison with optical spectra: (1) the far greater simplicity such as four (two are close doublets) principal K lines for iron, in comparison with hundreds of lines in the arc or spark spectrum; (2) the identical appearances of the series for all elements except the lightest, and the continuous and systematic variation of wave lengths with atomic number instead of a periodic relationship as for optical spectra. X-ray spectra and the Moseley law became the basis for proof of discovery of new chemical elements and for the derivation first of the Bohr theory and then of the modern vector model theory of the structure of atoms from hydrogen, number 1, up to element 102.

The analytical chemist, of course, had at his command a new and powerful method of qualitative and quantitative analysis, supplementing or superseding optical spectrography. However, there were inherent shortcomings which militated against widespread adoption and use in analytical laboratories; these shortcomings resided chiefly in the difficulties of preparing a target material from the unknown in a demountable tube, of providing a reliable source of electrons from a cold or hot cathode, and of laboriously pumping the tubes to requisite high vacua. Physicists were willing to undergo such difficulties in order to measure wave

lengths and derive theories of atomic structures, but chemists, except in rare instances, were unwilling to install and use such equipment when other less troublesome analytical methods were available.

Fluorescent X-Ray Spectrometry and Its Early Difficulties

Soon after the first primary spectra of beams excited by electrons in an x-ray tube were observed with the spectrometer, it was found that secondary fluorescent x-rays were excited in any material irradiated with beams of primary x-rays and that the spectra of these fluorescent x-rays were identical in wave lengths and relative intensities with those excited when the specimen is bombarded with electrons. Hence the characteristic emission spectrum is generated either by electron or x-ray photon excitation. The advantage was obvious of being able to irradiate any sample as a massive solid, powder, or liquid with a permanent sealed-off source of primary x-rays and then to analyze the fluorescent beam with the crystal spectrometer. Beginning in 1923, Hevesy, Coster, and others investigated in detail the possibilities of fluorescent x-ray spectroscopy as a means of qualitative and quantitative analysis, and Hevesy's book still remains a classic.²⁹ However, there was one apparently insuperable obstacle in the way of analytical usage—the extremely low intensity of the fluorescent rays, which made photographic exposures prohibitively long and fell below or at the very limit of sensitivity of the ionization chamber. The latter provides no amplification of ionization current resulting from ionization of gas molecules in the chamber. Thus for forty years analysis by fluorescent x-ray spectrometry was known as a potentially powerful but practically useless method.

The relative inefficiency of the fluorescence mechanism under the best conditions with the most modern high-intensity x-ray tubes with beryllium windows as primary source is such that the intensity of fluorescent radia-

tion from a copper radiator as a function of the voltage on a tungsten-target tube supplying primary rays is about 0.01 that of the tungsten rays, measured respectively at 5 cm from the radiator and 20 cm from the target. Today this secondary radiation is sufficiently intense for many applications such as microradiography; but for spectroscopic purposes must be added the fact that only a very small fraction of the total energy impinging upon the crystal in the spectrometer is diffracted and appears in the spectrum.

Improvements in Techniques and Instrumentation

X-Ray Tubes. In the face of such a discouraging prospect, three nearly simultaneous pathways of improvement were, and still are being, followed: (1) more intense primary x-rays, (2) more sensitive detectors, and (3) greatly improved optics of the spectrometer in terms of focusing crystals, multiple collimation slits or pinholes, and vacuum or helium tunnels for the rays from crystal to detector. The convergence of these developments in equipment and techniques has resulted in a success beyond all expectations, with the end not in sight.

The first of these contributing factors was the design and construction of x-ray tubes with beryllium-foil windows, such as the Machlett AEG-50 (operating in air) and OEG-50 (oil-immersed) tubes, which produce primary x-rays of intensity measured in millions of roentgens instead of the tens from earlier tubes. Consequently the intensity of excited fluorescent rays is amplified in proportion.

Detectors. The second factor was the perfection of the now familiar devices for detecting and measuring intensity of ionizing radiations, namely Geiger, proportional, and scintillation counters, all made possible by the great upsurge in electronics. Suffice it to say that ionization chambers, proportional and Geiger-counter tubes, consisting of a wire anode and sheet-metal cathode en-

closed in a glass envelope containing gas, differ essentially in the voltage across the electrodes. In the ionization chamber, which along with photographic blackening had to serve as detector and dosimeter of x-rays for thirty-five years, this voltage is low and the amplification factor is 1, that is, a 1:1 ratio of gas ions to x-ray photons. When used on the Bragg spectrometer, the ionization chamber was insufficiently sensitive for fluorescent spectral analysis. Over a range of a few hundred volts, the proportional counter operates by means of ionization avalanches, which may mean an amplification ratio of 10^6 .

At a sufficiently high voltage (usually 1100 to 1200 volts) the 1:1 correspondence between avalanches and primary ionization gives way to a new process, the excitation of short-wave length ultraviolet light which travels throughout the entire volume of gas and permits gas gains of 10^{10} in the Geiger counter. It combines high-quantum efficiency, simple construction, large signal amplitude, excellent stability, and very low background. It is limited to maximum counting rates of the order of several thousand per second. The proportional counter is capable of responding to very high counting rates, but this is accomplished at a great sacrifice of internal gains, thus high external pulse amplification is necessary.

In combination with a pulse amplitude analyzer* that discriminates between the characteristic radiation and the background

* Pulses are all amplified to a usable value with the same relative distribution of amplitudes. Then a minimum amplitude is selected and an electronic circuit (discriminator) is set so that amplitudes below this will not pass. Next a maximum amplitude is selected and a second electronic circuit is set to pass only amplitudes of this value or greater. Thus in operation a pulse below the minimum will not pass the first circuit and will be lost; one between the minimum and maximum amplitudes will pass the first circuit to the recorder; if above the maximum, it will pass both first and second circuits, generating 2 simultaneous pulses which are cancelled by anticoincidence and do not reach the recorder.

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radiation resulting from scattering and high order Bragg reflection, it provides resolution sufficient to separate the $K\alpha$ lines of neighboring elements in some cases, and those separated by 2 or 3 atomic numbers in others, and to register spectra from very small quantities of an element. The scintillation counter (employing alkali halide crystals containing thallium ions, or organic crystals such as anthracene, or even solutions such as terphenyl in xylene, together with multiplier phototubes to evaluate intensity of the light scintillations) is comparable to the Geiger counter in signal output and to the proportional counter in ability to count at a high rate. The signal-to-noise ratio is compared with that of the Geiger counter for soft x-rays, but much superior to both types of gas-filled tubes for hard x-rays. The scintillation counter provides spectral resolutions by means of pulse amplitude discrimination which is still perhaps a little inferior to that of the proportional counter but it is sensitive over the widest wave length range. The flowing proportional counter with a window so thin that gas must be kept flowing continuously through the tube, is superior for very long wave lengths.

The Design of Fluorescent X-Ray Spectrometers for Quantitative Analysis. For quantitative analysis, the accuracy

of a determination depends on the square root of the total number of counts measured^{39, 40}; for a standard deviation of 1% it is necessary to take 10,000 counts. It is obviously desirable to obtain these counts in the shortest time possible and therefore the optimum analyzing system is one designed to give the greatest x-ray intensity without sacrificing necessary resolution. The *intensity* is controlled by the exciting radiation, the geometric arrangement, the size and diffracting power of the analyzing crystal, and the efficiency of the counter components. The *resolution* is controlled by the perfection of the analyzing crystal and by the divergence allowed by slits or collimators defining the x-ray beam. This intensive study of the optics of the spectrometer is the third of the details of instrumentation which have contributed to the success of this method.

As an example the study by Birks, Brooks, and Friedman^{6a, 9} may be cited of reflection from a flat crystal, transmission through a curved crystal, reflection from a curved crystal, and double-crystal reflection.

Figure 1 illustrates diagrammatically the first of these methods. Primary radiation from the x-ray tube strikes the specimen, which may be in the form of a solid, a powder, or a liquid. The fluorescent radiation

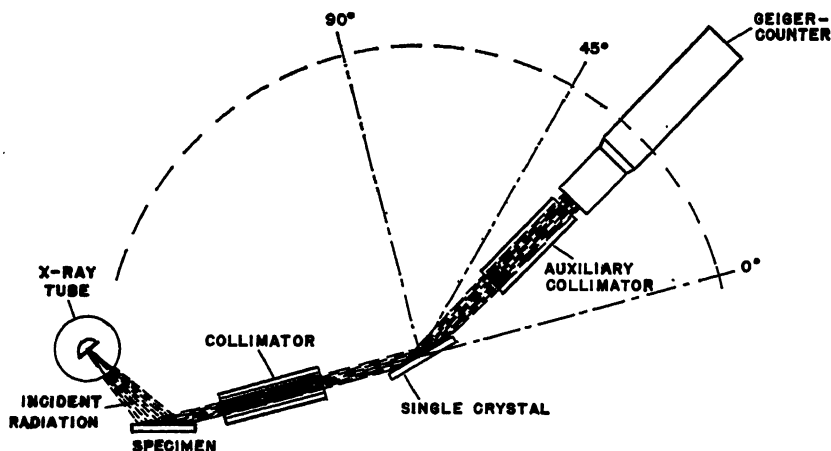


FIG. 1. Diagram of one type of x-ray fluorescence spectrometer.

emerging in all directions is collimated into a parallel beam of polychromatic radiation which strikes the analyzing crystal and is spread out into a spectrum in accordance with the Bragg law. The entire matter of the optical geometry of spectrometers is covered in the new book by Birks,^{6a} and in the companion article by Birks in this Encyclopedia.

The Choice of Crystal Analyzers. Many crystals have been tried as analyzers, especially for the flat crystal technique. Sodium chloride is most frequently used though lithium fluoride and aluminum give somewhat greater intensities; curved aluminum crystals have been successfully used instead of mica. The primary concern is with the range of wave lengths to be measured. No particular complications are involved in elements titanium (atomic number 22) to uranium (atomic number 92) since the characteristic rays may have air paths without serious absorption. In the range magnesium (atomic number 12), which has a $K\alpha$ wave length of 9.889 Å to titanium²² with a $K\alpha_1$ wave length of 2.7481 Å, the vacuum- or helium-tunnel spectrometer must be employed together with special precautions in collimation, focusing, thinner windows for Geiger tubes, sample preparations, and choice of analyzing crystal. For magnesium,¹² aluminum,¹³ and silicon¹⁴ gypsum has given greatest intensity, and for phosphorus¹⁵ to titanium²² potassium iodide and potassium chloride crystals give appreciably better intensity. From the Bragg law it is evident that the maximum wave length that may be diffracted is $2d$; hence crystals of greater d spacing the lower the atomic number are required. The most suitable crystal at present for aluminum to phosphorus is ethylenediamine d -tartrate ($2d = 8.76$ Å.)

Differential Analyses at Controlled Voltages. Even with the relative simplicity of x-ray spectra some complications still remain in overlapping lines, effects of characteristic absorption edges where several ele-

ments may be present in the sample such that one fluorescent ray will excite another and thus lead to difficulties in quantitative analysis. In order to excite fluorescent radiation, for example the K series, it is necessary for the primary beam to be generated at or above a critical voltage V defined by $V = hc/e\lambda_{K_{abs}}$ where $\lambda_{K_{abs}}$ is the wave length of the K absorption edge of the fluorescent element and h , c , and e are the usual constants, or $V = 12400/\lambda_{K_{abs}}$. It is obvious that by careful control of V for the primary beam the K or L series lines of elements in a mixture can be generated separately or in groups at will and thus can produce improved stepwise resolution and simplification of interpretation.

Quantitative Analyses From Line Intensities and Intensity Ratios With Internal Standards

For quantitative analysis of mixtures by fluorescent x-ray spectrometry it is obvious that the relationship between intensity, measured photographically or with a counter, and amount of element sought must be established. As is familiar practice in optical spectrography the usual procedure is to set up calibration curves for intensity versus amount of element present from known standards. In most cases the ratio of the intensity of a characteristic line (such as $K\alpha$) for the element being analyzed to that of a line in the same range of wave lengths for a known element serving as an internal standard is plotted as a function of composition from standard homogeneous samples of known composition. For example, Clark and Terford¹⁷ prepared a calibration curve for analysis of iron in dusts from known mixtures of iron and nickel and plotted the ratios $I(FeK\alpha)/I(NiK\alpha)$ against percentage of iron. Techniques and examples are fully discussed in the companion article by Wittig and in the book by Birks.^{6a}

Recently a great deal of attention has been directed to the complications of interelement

and matrix effects in binary and multicomponent systems both experimentally and theoretically as it affects departures from linear relationships of intensities or intensity ratios to percentage composition. A fluorescent intensity I_f value can be expressed as $I_f = F(C_i, \mu_i, \lambda_i, \lambda_f)$, or a function F (which of course involves instrumental geometry, detector sensitivity and other variables which are fairly constant in a given spectrometer) of the concentrations of all the elements in the sample. C_i , the mass absorption coefficients of these elements, μ , and the wave lengths of the incident, λ_i (whether monochromatic or polychromatic) and the measured fluorescent beams, λ_f .

Sherman⁵¹ first derived rigorous equations which have been adapted and modified by other workers¹¹ from which curves could be constructed for the matrix effect of elements of various atomic numbers, and these curves then compared with experimental calibration curves for known mixtures. In this way Hunt⁵¹ has made analyses of lignite ores for uranium, thorium and molybdenum in matrices of iron, calcium, and magnesium. Using probability theory and the theory of errors precision in x-ray emission spectrography can be controlled even with significant background.⁵⁴ A very significant approach to the matrix problem is found in the companion article by Mitchell.

A matrix dilution technique, in which a sample is blended with cornstarch and LiCO_3 , is in effective industrial use.²⁵ Coherent and Compton scattering of primary x-rays which produce background are of special importance in low atomic number elements³²; but actually the scattering radiation may be used as an internal standard in quantitative analysis from intensities of characteristic spectrum lines.² Another solution of the matrix problem recently suggested is to extrapolate fluorescent-intensity ratios in binary systems to zero sample thickness.²⁸ Filter papers are impregnated with a solution of the sample and dried;

measurements are made with 1, 2, 3 and more layers, the intensities of a given spectrum line then being plotted against the number of layers and extrapolated to zero.

Multichannel Recording

One of the greatest aids to improved speed and accuracy in optical spectroscopy was the development by Applied Research Laboratories, Glendale, Cal. of the Quantometer, or multichannel recording, which involves the ratio system of unknown to known standards and thus simultaneous analysis of as many as 20 elements. It was quite logical to extend the same techniques to fluorescent x-ray analysis by means of counter tubes. Actually two systems are involved: the dispersive multichannel utilizing a number of crystal analyzers set at correct Bragg angles for the $K\alpha$ or $L\alpha$ lines of several elements in the specimen (the same result is accomplished with a single spectrometer which moves automatically from one fixed position to another); and the nondispersive, utilizing filters.²⁷ The latter may be illustrated by the analysis of an aluminum alloy containing zinc, copper, and magnesium. The nondispersive analyzer is set up for analysis of zinc and copper. A filter of 0.0045-in. copper sheet was used in the zinc channel (to a Geiger counter) to absorb radiation shorter than 1.4 Å, but transmitting copper and zinc K-radiation. A filter of 0.0030-in. nickel sheet is used in the copper channel to absorb the zinc K-radiation. A third channel has an external standard and a 0.0030-in. copper filter. Working curves were made from alloy with varying copper and fixed zinc and with varying zinc and fixed copper. Two channel ratios are recorded and each corrected by an amount depending on the reading on the other.

Applications

According to Birks,^{6a} there are 12 groups of applications depending upon physical state of the specimen, wave length range of

x-rays, and the concentrations of elements: (1) alloys; (2) minerals and ores; (3) powders; (4) glass and ceramics; (5) liquids; (6) plating; (7) inhomogeneous specimens; (8) low concentrations; (9) limited total quantity; (10) light elements; (11) dynamic systems; (12) continuous process control.

Major Constituents

Alloys. In the analysis for elements present in amount from several per cent up to 100 per cent, fluorescence analysis has the greatest advantage over optical spectrographic analysis. Values correct to a fraction of 1% for counting times less than 1 min. are commonly obtained in spite of some of the complications of calibration. Analyses are made on solids, many in solutions or extracted residues. Invariably the fluorescent method is more rapid, more accurate, and more economical in terms of man-hours than spectrochemical or wet-chemical methods. Among these are routine analyses of high-temperature steels for uranium, chromium, cobalt, iron, molybdenum, and nickel. Several practical metallurgical applications in the research laboratories of one of the large steel companies are reported by Koh and Caugherty.³⁷ Some of the most recent examples of alloy analyses may be found in references 38, 52, 30, 34, 3 ("Zircaloy"). This field is ably covered in the companion article by Wittig, p. 726.

Analysis of Surface Films. In view of the fact that the minimum effective thickness of a metallic element to produce maximum fluorescent yield is very low, the analysis is an excellent means of observing chemical change on or near the surface, thus supplementing the electron diffraction method.⁵⁰ This has been applied to the study of oxide films formed on alloys at elevated temperatures. Thus in iron-chromium alloys there is an impoverished chromium content in layers next to the oxide-film boundary, then a chromium-rich layer next to the unoxidized metal. For substitutional solid solutions dif-

fraction patterns alone may be insufficient for identification since crystal spacings may not be changed; the fluorescence analysis, of course, will detect all elements present. For example, a bromine extract from type-347 stainless steel gave a diffraction pattern only for columbium carbide; the fluorescence spectrum showed chromium, iron, nickel, tungsten, and bromine besides columbium.³⁷

Minerals. The fluorescent x-ray spectrometer is being widely used by the Bureau of Mines and many other laboratories for analyzing a variety of minerals and ores ranging from high-purity minerals to low-grade ores, including mineral-dressing products obtained in the beneficiation of such ores. Examples are selenium in pyrite (bromine forms a good standard for selenium and vice versa) and sulfur and thorium in monazite; perhaps most exhaustively studied are the analyses of hafnium-zirconium and niobium-tantalum systems in ores,^{6, 12, 15, 45} for which chemical analyses are extremely difficult, requiring from 5 to 15 days. Examples from the field of ceramics are given by Patrick⁴⁷; and barite by Gulbranson.²⁴ Recent examples, all published in *Analytical Chemistry*, illustrate the wide range of minerals, ores and manufactured inorganic products which are successfully, rapidly and economically analyzed by x-ray emission spectrometry: strontium⁴²; cesium and rubidium⁴; uranium and thorium (frequently reported in trace amounts)^{1, 49}; yttrium and other rare earths^{28, 43}; tungsten and molybdenum²²; tantalum, niobium, iron and titanium oxide mixtures⁴⁴; four major phases of Portland cement¹⁸; aluminum, silicon and iron in flotation products of clays and bauxites.⁵³

Powders (pigments, abrasives, dusts). While the analysis by means of x-ray diffraction of mining and foundry dusts for crystalline α -quartz, which is responsible for the serious pathological lung condition silicosis, has been in successful use for several years, nothing has been done to devise a method of

analysis of such dusts for iron, which may be responsible for the lung condition known as siderosis, supposedly benign but actually capable of developing into nodules and simulating the appearance of silicosis in diagnostic lung radiographs. Since the iron in dusts is not indicated in diffraction patterns owing to amorphous conditions, it has been necessary to resort to very laborious and inaccurate chemical analyses. Clark and Terford¹⁷ found the fluorescent spectral analyses remarkably successful in the analyses of dusts from all parts of a large steel foundry. With the same samples the same basic Geiger unit was used as a diffractometer to determine quartz quantitatively by diffraction and as a spectrometer to determine iron. Powdered nickel served satisfactorily as an internal standard for both. A strictly linear working calibration curve of $I_{FeK\alpha}/I_{NiK\alpha}$ against percentage of iron holds up to the maximum amount of iron found in any dust, about 30 %. For a large number of dusts collected in various areas the amounts of silica and of iron vary inversely.

Minor Constituents

As the amount of a constituent undergoing analysis decreases it is evident that for maintaining accuracy the counting times must be increased. Under these conditions linear calibration curves can usually be obtained and a wide range of useful analyses made with potential applications to many chemical, medical, biological and industrial problems. Some reported analyses are:

Iron in the hemoglobin of blood (average 12 mg/100 ml), compared with the usual color match of a diluted blood sample with color standards. The accuracy is $\pm 5\%$, which is improved by the use of samples larger than 0.3 ml.⁷ Urinalysis is another application.

Analyses in the Petroleum Industry. Lead and bromine in gasoline¹⁰ are simultaneously determined with liquid samples. The $L\alpha$ line of lead at 1.17 Å and the $K\alpha$ line

of bromine (present in ethyl fluid as ethylene dibromide) are used. Geiger counts of 1 min on the peak of the lead line gave a probable error of ± 0.06 ml/gal. in a content of 4 ml of tetraethyllead/gal. of gasoline, and for bromine ± 0.16 ml/gal. in 1.8 ml of ethylene dibromide/gal. of gasoline, and for bromine ± 0.16 ml/gal. in 1.8 ml of ethylene dibromide/gal. of gasoline. This analysis is particularly interesting since it has been compared most favorably with chemical methods, polarography, and x-ray absorption photometry. Fluorescence analysis has the great advantage that variation in the gasoline base stock of presence of additives such as chlorine have negligible effects. The method has been further critically studied as to the matrix effect and improved so that an average error of ± 0.026 ml/gal. is achieved in times as short as 5 min. per sample.¹⁸

With the advent of new anti-knock agents for gasoline and additives for lubricating oils the petroleum industry relies heavily upon fluorescence analysis, not only for ethyl fluid but also for metallo-organic compounds containing nickel,²⁰ manganese,²¹ and others. As a matter of fact briquetted organo-metallic precipitates are the basis of a powerful general method of analysis.²¹ Sulfur in oil is a similar analysis which can be made equally well by x-ray fluorescence emission analysis (a vacuum or helium path is needed for element 16) and by x-ray absorption, especially from a Fe^{55} K-capture source¹⁹; the former is freer from interference, the latter is less costly. Vanadium, iron and nickel in traces are directly obtained in 4 ml. samples of oil without ashing or concentrating to ± 1 ppm in an outstanding 1960 contribution.²² The assay of platinum in aluminum base reforming catalyst is done very rapidly with an accuracy comparing favorably with spectrophotometric results.⁴¹

As an illustration of other analyses may be cited the Bureau of Mines analyses of germanium in coal and coal ash (100 per day)¹⁴; iodide in photographic processing

solutions at the Eastern Kodak Co.⁴⁶; nickel flashings on porcelain enamels (0.015 to 0.070 mg/sq ft easily determined).⁴⁷

Microanalyses

It has been a matter of interest to discover how well fluorescent x-ray spectral analyses can compete with optical spectroscopy in detecting trace amounts of elements. By a technique resembling that of the familiar spot test, it was shown that 15.6 counts/sec above background of $\text{ZnK}\alpha$ radiation per microgram on filter paper could be measured. A counting time of only 2 min. is required to detect $\frac{1}{80}$ μg of zinc. Absorption effects are eliminated in such thin samples since 1 μg of zinc spread over 1 sq cm is only 3 atoms, or 10 Å, thick. The same technique is successfully used for determinations of microquantities of vanadium, copper, iron, silver, bromine, gold, and lead. Exceptionally promising is the microanalysis of thin sections of biological tissue.²⁶ By means of comparison between the intensity of a given spectral line from the specimens and the intensity of the same line from a similar specimen with a known quantity of element per unit of surface, the unknown is evaluated. Distinct zinc peaks were produced with only 0.2% of zinc in the area of a thin microtome section of pancreas 200 μ thick and a similar amount of iron in a spleen section 80 μ thick.

Traces of vanadium, iron and nickel in liquid oil are determined down to several ppm as noted above.⁴⁸ Palladium, platinum, rhodium and iridium are rapidly determined in solutions with sensitivities of detections of 0.10, 0.20, 0.14 and 0.02 mg/ml, respectively. Microgram quantities of K ions liberated by ground mica are extracted on ion exchange membranes and the analysis run on a small rectangle.⁴⁹ Thus with improvement of sensitivity of detectors and pulse amplitude discrimination to clearly differentiate faint spectrum lines from background fluorescent emission spectroscopy has reached the stage of detecting traces in parts

per million where up to 1957 it was only parts per 10,000.

Measurement of Plating Thickness

Fluorescent x-ray spectroscopy has found one of its best practical applications in the determination of plating thickness. Where, for example, silver-plated copper is excited, the fluorescent copper rays could be partly absorbed by the silver plating. A measurement of this reduction in intensity, or of the $\text{AgK}\alpha$ intensity, leads to a direct measurement of thickness. Calibration curves may be calculated directly from known absorption coefficients for single plating layers. Families of curves may be found for double or more plating layers. The application of this technique to tin plating on steel has been adopted by the industry recently and is in perhaps the largest scale use of any of the applications.^{5, 48}

Dynamic Systems^{5a}

Representative of the rapid progress in fluorescence spectrometric analysis is the evaluation of variation in composition in dynamic systems, or a new dimension added to analytical techniques such as (1) rate of solution of solids in solids or solids in liquids; (2) rate of mixing of liquids; (3) rate of precipitation from solution; (4) diffusion of metals during phase transformations; (5) rate of corrosion of surfaces; (6) rate of sublimation. A cumulative Gaussian curve for the rate of solution of CuSO_4 in water is described by Birks.^{6a} An excellent example is the measurement of arsenic and antimony in lead by formation of the oxides (insoluble in lead) on the surface of the lead.

REFERENCES

1. ADLER, I., AND AXELROD, J. M., *Anal. Chem.*, **27**, 1002 (1955).
2. ANDERMANN, G., AND KEMP, J. W., *Anal. Chem.*, **30**, 1306 (1958).
3. ASHLEY, R. W., AND JONES, R. W., *Anal. Chem.*, **31**, 1632 (1959).

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4. AXELROD, J. M., AND ADLER, I., *Anal. Chem.*, **29**, 1280 (1957).
5. BEEGHLY, H. F., *J. Electrochem. Soc.*, **97**, 152 (1952).
- 6a. BIRKS, L. S., "X-Ray Spectrochemical Analysis," Interscience Publishers, N. Y., 1960, pp. 137.
- 6b. BIRKS, L. S., AND BROOKS, E. J., *Anal. Chem.*, **22**, 1017 (1950).
7. BIRKS, L. S., AND BROOKS, E. J., *Naval Res. Lab. Rept.* 3367 (1951).
8. BIRKS, L. S., AND BROOKS, E. J., *Anal. Chem.*, **23**, 707 (1951).
9. BIRKS, L. S., BROOKS, E. J., AND FRIEDMAN, H., *Anal. Chem.*, **25**, 692 (1953); **27**, 437 (1955).
10. BIRKS, L. S., BROOKS, E. J., FRIEDMAN, H., AND ROE, J., *Anal. Chem.*, **22**, 1208 (1950).
11. BURNEAM, H. H., HOWER, J., AND JONES, L. C., *Anal. Chem.* **29**, 1827 (1957).
12. CAMPBELL, W. J., AND CARL, H. F., *Anal. Chem.*, **26**, 800 (1954).
13. CAMPBELL, W. J., AND CARL, H. F., *Anal. Chem.*, **27**, 1884 (1955).
14. CAMPBELL, W. J., CARL, H. F., AND WHITE, D. E., *Anal. Chem.*, **29**, 1009 (1957).
15. CARL, H. F., AND CAMPBELL, W. J., *ASTM Spec. Tech. Publ. No. 157*, 63 (1953).
16. CLARK, G. L., "Applied X-Rays," 4th ed., McGraw-Hill Book Co., N. Y., pp. 109-160, 1955.
17. CLARK, G. L., AND TERFORD, H. C., *Anal. Chem.*, **26**, 1416 (1954).
18. COPELAND, L. E., BRUNAUER, S., KANTRO, D. L., SCHULZ, E. G., AND WEISE, C. H., *Anal. Chem.*, **31**, 1521 (1959).
19. DOUGHMAN, W. R., SULLIVAN, A. P., AND HIRT, R. C., *Anal. Chem.*, **30**, 1924 (1958).
20. DURGGINS, C. W., AND DUNNING, H. N., *Anal. Chem.*, **21**, 1040 (1959).
21. FAGEL, J. E., BALIS, E. A., AND BRONK, L. A., *Anal. Chem.*, **29**, 1287 (1957).
22. FAGEL, J. E., LIEBHAFSKY, H. A., AND ZEMANY, P. D., *Anal. Chem.*, **30**, 1918 (1958).
23. FELTEN, E. J., FANKUCHEN, I., AND STEIGMAN, J., *Anal. Chem.*, **31**, 1771 (1959).
24. GULBRANSON, L. B., *Anal. Chem.*, **27**, 1181 (1955).
25. GRIMM, E. L., *Anal. Chem.*, **29**, 1821 (1957).
26. HAMOS, L. VON, AND ENGSTROM, A., *Acta Radiol.*, **25**, 325 (1944).
27. HASTER, M. F., AND KEMP, J. W., *ASTM Spec. Tech. Publ.*, No. 157, 34 (1953).
28. HEIDEL, R. H., AND FASSEL, V. A., *Anal. Chem.*, **30**, 176 (1958).
29. HEVESTY, G. VON, "Chemical Analysis by X-Rays and its Applications," McGraw-Hill, N. Y., 1932.
30. HOUK, W. W., AND SILVERMAN, L., *Anal. Chem.*, **31**, 1069 (1959).
31. HUNT, R. H., Ph.D. thesis, Univ. Ill., 1959.
32. JOHNSON, C. M., AND STOUT, P. R., *Anal. Chem.*, **30**, 1921 (1958).
33. JONES, R. A., *Anal. Chem.*, **31**, 1341 (1959).
34. JONES, R. W., AND ASHLEY, R. W., *Anal. Chem.*, **31**, 1629 (1959).
35. KANG, C.-C., KEEL, E. W., AND SOLOMON, E., *Anal. Chem.*, **32**, 221 (1960).
36. KING, A. G., AND DUNTON, P., *Science*, **122**, 72 (1955).
37. KOH, P. K., AND CAUGHERTY, B., *J. Appl. Phys.*, **23**, 427, 698 (1952).
38. LAMB, F. W., NIEBYLSKI, L. M., AND KIEFER, E. W., *Anal. Chem.*, **27**, 129 (1955).
39. LIEBHAFSKY, H., *Anal. Chem.*, **26**, 26 (1954); **28**, 583 (1956).
40. LIEBHAFSKY, H. A., PFEIFFER, H. G., AND ZEMANY, P. D., *Anal. Chem.*, **27**, 1257 (1955).
41. LINCOLN, A. J., AND DAVIS, E. N., *Anal. Chem.*, **31**, 1317 (1959).
42. LUCCHESI, C. A., *Anal. Chem.*, **29**, 370 (1957).
43. LYTLE, F. W., AND HEADY, H. H., *Anal. Chem.*, **31**, 809 (1959).
44. MITCHELL, B. J., *Anal. Chem.*, **30**, 1894 (1958).
45. MORTIMORE, D. M., AND ROMANS, P. A., *J. Opt. Soc. Am.*, **42**, 673 (1952); *Norelco Repr.*, **1**, 107 (1954).
46. OWEERBACH, D., HOEFFER, R. T., AND KLEM, H. J., *Anal. Chem.*, **31**, 579 (1959).
47. PATRICK, R. F., *J. Am. Ceram. Soc.*, **35**, 189 (1952).
48. PELISSIER, G. E., *Elec. Mfg.*, **49**, 124 (1952).
49. PISE, G., AND HUFFMAN, A. A., *Anal. Chem.*, **27**, 1875 (1955).
50. RHODIN, T. N., *Anal. Chem.*, **27**, 1857 (1955).
51. SHERMAN, J., *ASTM Spec. Tech. Publ. No. 157*, 27 (1953).
52. SILVERMAN, L., HOUK, W. W., AND MOUDY, L., *Anal. Chem.*, **29**, 1762 (1957).
53. SUN, S.-C., *Anal. Chem.*, **31**, 1822 (1959).
54. ZEMANY, P. D., PFEIFFER, H. G., AND LIEBHAFSKY, R. A., *Anal. Chem.*, **31**, 1776 (1959).
55. ZEMANY, P. D., WELBON, W. W., AND GAINES, G. L., *Anal. Chem.*, **30**, 299 (1958).

G. L. CLARK

FLUORESCENCE SPECTRA APPLICATIONS

The speed, sensitivity, and precision of x-ray fluorescence analysis for substances of varied composition and physical structure

place this technique in the forefront of modern methods of instrumental analysis. The scope of applications in industry, government, and research institutions continues to increase at a steady rate. The fact that the technique is inherently non-destructive or does not deface the specimen lends attractiveness to it in instances where specialized analysis is needed. The relative simplicity of the fluorescent spectrum, as contrasted for example with optical emission, provides distinct advantages in its interpretation.

The fluorescent x-rays emitted by a material and used for its analysis are generated by directing a primary beam of high energy x-rays against it. The x-ray photons of the high energy beam are absorbed by the material. Using the Bohr concept of atomic structure, when an atom in a material is given sufficient energy by absorbing these photons, an electron may be ejected from one or more of its inner shells. The place of the electron is immediately filled by an electron from an outer shell, whose position in turn will be filled by an electron even further out, etc. In this manner the atom returns to its normal energy state by a series of steps in electron transitions. For each of these steps an x-ray photon is emitted. Since each of these steps is discrete and characteristic, the energy or wavelength of each photon may be used as a unique means of characterizing the element in the material.

The fluorescent x-rays generated from a sample provide an unequivocal identification of the elements in it and their intensity measurement, an index of the amount of each present. In most applications, however, this measurement is not straightforward because the fluorescent intensity often is not directly proportional to the concentration of the element which gives rise to it. Basically, this non-linear property is attributable to fundamental x-ray-matter interaction effects which take place in a substance between the component elements themselves.

The effects of interaction—variously

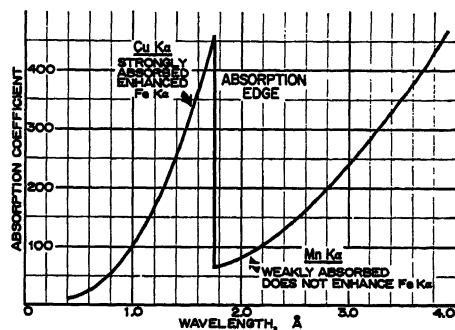


FIG. 1. Absorption coefficient of iron and its interaction properties with copper and manganese.

called absorption and enhancement, matrix, self-absorption, or interelemental effects—are well-known; the interaction between copper and iron in the same specimen provides a classic example. In Figure 1 is shown the absorption coefficient of iron plotted against wavelength. The absorption edge of iron is at 1.739 Å and the $K\alpha$ emission line of copper is at 1.537 Å. The 1.537 Å copper radiation, occurring on the short wavelength side of the iron absorption edge, will be strongly absorbed by iron. This absorbed radiation will excite and further enhance the characteristic radiation of iron over that generated by the primary exciting beam. If manganese rather than copper coexists with iron, the interaction effects are much less pronounced. The manganese $K\alpha$ line occurs at 2.098 Å, on the long wavelength side of the iron absorption edge, and therefore is not strongly absorbed. Similarly, the iron $K\alpha$ line at 1.932 Å, on the long wavelength side of the manganese absorption edge at 1.892 Å, does not enhance manganese.

Corrections for Interaction

Several practical methods have been developed to cope with interaction problems. The better known of these methods are the following:

Dilution. Generally, the substance to be analyzed is diluted in high ratio with a substance which is relatively transparent to

x-rays. Substances such as carbon, water, starch, lithium carbonate, borate glass, and oxides of the low atomic number metals have been successfully used as diluents. The degree of dilution required to minimize or eliminate interaction can be calculated by use of the absorption constants of the specific material, or it can be determined by experiment.

Mathematical Correction. Where elements can be measured both as isolated and as coexisting forms, in which they are contained in varying ratios as in alloys, empirical corrections for interaction may be derived which provide accurate results.¹ Sherman² has further considered the problem of interaction from the theoretical standpoint of the fundamental absorption and emission properties of the elements. Although his results are most encouraging, the derivations of mathematical expressions which describe this intricate phenomenon and the solutions involved in practical applications thereof are fairly complicated.

External Standards. The use of a number of reference standards which closely simulate the various compositions to be analyzed enables compensation for interaction effects to be made. A family of calibration curves often is helpful for this purpose. The chief disadvantage of this method is that the reference standards must be periodically interspersed with the unknowns during

measurement. This, of course, adds to the time and effort required for analysis.

Internal Standard. A fixed ratio of an added element in a sample can be used as an internal standard. This is probably the best-known method used to compensate for interaction.³ The similarity in spectral behavior of the sought to the added element and the ultimate homogeneity of both in the blend are factors of paramount importance. For powdered solids there is ample evidence that reduction in average particle size to values as low as a few microns often is necessary to obtain maximum intensity and precision of measurements. Particle reduction is especially critical for fluorescence of low atomic number elements for which the sample penetration depth is very small.

Sensitivity

The sensitivity of x-ray fluorescence applied to varied substances is highly dependent upon the substrate or matrix and the nature of the element measured therein. Generally, the sensitivity varies directly with the atomic number of the element and inversely with the atomic number of the matrix in which it is measured. As an example, 10 parts per million of iron can readily be detected in cellulose or hydrocarbons. Matrices of higher atomic number, such as titanium which is more absorbing, lower the iron sensitivity by about two orders of magnitude.

The decrease in fluorescent sensitivity for the measured element with atomic number is associated with two fundamental physical properties. First, the decrease in atomic number results in the production of longer and hence more easily absorbed characteristic wavelengths. Second, the fluorescent yield or probability of emission function of the element decreases with atomic number. A plot showing the dependence of fluorescence yield upon atomic number is shown in Figure 2.⁴ To exemplify this second property, the fluorescent yield of iron [26] is

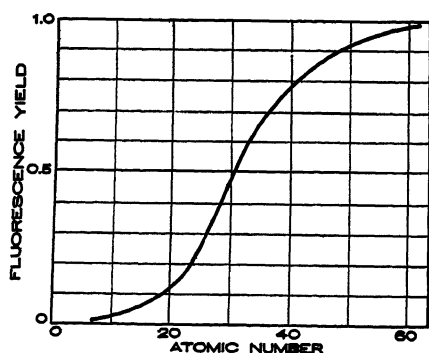


FIG. 2. Dependence of fluorescence yield upon atomic number.

about three times that of calcium [20]. This, with the property of being more easily absorbed, lowers the absolute sensitivity for calcium to a level considerably below that for iron in most substances.

In general, x-ray fluorescence with conventional instruments does not possess nearly the absolute sensitivity of emission spectrographic detection, which is of the order of 10^{-9} gram for a number of the elements. However, under favorable circumstances fluorescence can be applied in the detection and measurement of microgram quantities of certain elements. High sensitivity methods employing conventional equipment have been applied in a number of cases to the determination of elements having atomic numbers greater than 20 which occur in low atomic number matrices; these include biological tissues, organic films, fibers, or similar low absorbing media.

Nickel, iron, and vanadium deposited by evaporation from solution onto a small filter paper circle can readily be determined in the range of 1 to 50 micrograms. The relative error is about two per cent where cobalt is used as an internal standard and helium is passed through the optical path to minimize absorption loss. The calibrations are linear, indicating negligible effects of elemental interaction. Figure 3 illustrates a calibration for nickel in the microgram range.

A brief survey of the literature for specific applications of x-ray fluorescence readily indicates that the scope and variety of this technique are relatively large. Accordingly, the following examples illustrate only a selected number of these applications.

Metals

Historically, the metals industry has been in the forefront of the development and applications of x-ray fluorescence. These achievements make possible the analysis of most all metal alloys—both ferrous and non-ferrous, in major or minor concentrations—

with precisions as good or better than those obtained by conventional chemical methods, but at a fraction of the cost in time and effort. Thus, the techniques of metal analysis are substantially in a well-developed state.

In the foregoing discussion on corrections for interaction effects, it was pointed out that experimental data could be employed in performing mathematical corrections for these effects.¹ In Table 1, x-ray and chemical values obtained in the analysis of alloys are compared. Where proportional intensities were used directly in the interpretation, the x-ray results were in considerable error for most all values; but after correcting for interaction, the agreement between chemical and x-ray results became excellent in practically every case.

A relatively inexpensive, portable x-ray fluorescence spectrograph weighing less than 100 pounds, developed by Philips Electronics, Mount Vernon, New York, is commercially available for plant process control of metals and alloys. The intensity necessary for exciting the fluorescent spectrum is generated by a special high emission x-ray tube which employs a beryllium disc sputtered with gold to serve both as the target and the end window for the x-rays.

The x-ray fluorescence probe spectrograph developed by Castaing and Guinier⁵ has provided a new dimension for the investigation of micro grain and phase boundary com-

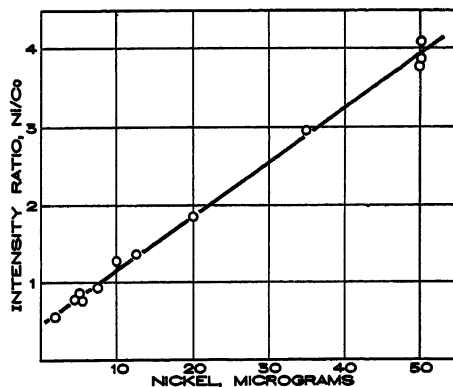


FIG. 3. Calibration for nickel on filter paper.

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TABLE 1. ANALYSIS OF ALLOYS

Alloy	Element	Chemical %	X-ray		X-ray	
			Corrected for Interaction %	% Error	Proportional Intensities %	% Error
1	Cr	19.85	20.29	2.22	27.7	39.5
	Fe	65.94	65.95	0.0	52.1	21.0
	Ni	13.98	13.76	1.57	6.98	50.0
2	Cr	21.23	20.39	3.95	28.7	35.2
	Fe	13.85	15.04	8.60	15.1	9.0
	Ni	64.84	64.57	0.42	46.5	28.3
3	Cr	32.13	32.44	0.97	40.4	25.8
	Fe	35.43	35.86	1.21	27.3	22.9
	Ni	31.86	31.66	0.63	18.6	41.5
4	Cr	16.45	16.96	3.10	19.8	20.4
	Fe	50.20	51.35	2.29	81.0	61.4
	Ni	26.80	25.54	4.70	15.1	43.6
	Mo	6.55	6.15	6.10	6.52	0.5
5	Cr	18.43	19.63	6.51	24.9	35.1
	Fe	66.26	64.93	3.01	51.5	22.3
	Ni	12.99	13.23	1.85	6.79	48.4
	Mo	2.32	2.22	4.31	2.42	4.3

positions of metals. In this instrument the sample itself serves as the target against which a high potential needle-like stream of electrons—the probe—impinge to generate the fluorescent x-rays. A point-by-point microanalysis may be performed in which the solid phase composition of one cubic micron, i.e., about 10^{-11} gram, is determined at each probe point. Refinements in the instrumentation of this specialized device, as well as increases in the variety of its applications by metallurgists, are being made.

Non-Metals

The detection and determination of several low atomic number non-metals by x-ray fluorescence have been reported. These have been achieved mostly because of improvements made in recent years in detectors and their associated electronic components. In particular, the use of proportional counters—static and flow, with suitable channels for

pulse height discrimination—has made possible the detection of non-metals in the third period of the Periodic Chart.

X-ray fluorescence has been applied to the routine determination of chlorine in vinyl resins in which this non-metal is a major component.⁶ A Geiger-Muller counter provides adequate sensitivity in this application, provided helium is passed through the optical path. The calibration sensitivity for chlorine $K\alpha$ radiation in this substance, which contains carbon and hydrogen as the other components, is 10 counts per second for one per cent chlorine in the concentration range of 55 to 75 per cent. The estimated precision is one part per thousand.

Methods for the determination of sulfur in hydrocarbons in concentrations below one per cent have been developed.⁷ This requires the use of flow proportional counting, pulse height discrimination to accept the low energy characteristic sulfur radiation and to reject most of the unwanted high energy x-rays, and the use of helium in the optical path to minimize absorption loss. The results obtained by x-ray measurement compare favorably in precision and accuracy with conventional lamp, bomb, or furnace methods. A measuring time of only about 10 minutes is required for x-ray analysis in comparison with much longer times for the other methods.

Phosphorus and silicon, also in period three, have been determined by x-ray fluorescence under adverse conditions from the standpoint of the matrices in which they were measured. Both have been measured in ceramic materials and slags in which large absorption or interaction effects occur. In slags⁸ the precision for phosphorus at the one per cent concentration level was 0.07 per cent; that for silicon at the 20 per cent level was 0.4 per cent.

Petroleum

Applications of x-ray fluorescence in the processing and refining of petroleum prod-

ucts fall into two categories: the analysis of materials which are intermediate in or incidental to the steps of manufacture, and those employed for inspection and control of finished products. The variety in composition, concentration range, and phase of these materials exacts broad versatility in the x-ray applications.

X-ray fluorescence has been applied in the analysis of gasoline for additive elements. Tetraethyl lead in concentrations of 0.1 to 6 milliliters per gallon has been determined with an average of ± 0.026 milliliters per gallon.⁹ Because of matrix differences, corrections based on the carbon-hydrogen ratio must be established to obtain accurate results. Additive manganese also has been determined in gasoline in the concentration range of 0.1 to 1.0 gram per gallon.¹⁰ Elemental iron, which in this specific method comprises a part of the instrumental setup, serves as a compensative reference. In addition to eliminating matrix effects, the reference improves precision to a confidence level of 99 per cent.

X-ray fluorescence has been used to determine barium, calcium, and zinc in lubricating oils.¹¹ This technique was found to be at least equal in accuracy to chemical methods for these elements in concentration ranges of a few tenths per cent.

The concentration of both minor and trace elements in catalysts has been determined by x-ray fluorescence measurement. Accurate measurements have been made of trace amounts of iron, nickel, and vanadium in silica-alumina cracking catalyst¹² and of platinum in alumina-base reforming catalyst.¹³ The agreement between chemical-spectrophotometric and x-ray results for platinum in the latter is illustrated in Table 2. The average relative difference between methods is one per cent. With catalytic substances of these compositions, the measurements of minor or trace amounts of elements are essentially free of interference produced by matrix differences,

TABLE 2. ANALYSIS OF REFORMING CATALYST

Sample No.	Platinum, %		
	Spectrophotometric	X-ray Fluorescence	Difference
1	0.592	0.583	0.009
2	0.587	0.590	0.003
3	0.585	0.582	0.003
4	0.581	0.583	0.002
5	0.575	0.575	0.000
6	0.571	0.582	0.011
7	0.586	0.575	0.011
8	0.583	0.573	0.010
9	0.587	0.581	0.006
10	0.583	0.584	0.001
11	0.586	0.574	0.012
12	0.589	0.586	0.003
			Av. 0.006

Minerals

X-ray fluorescence has been particularly useful in the analysis of rare earth minerals, thus avoiding many of the difficulties inherent in chemical methods.

Thorium has been determined in minerals using thallium as the internal standard.¹⁴ A comparison of x-ray with chemical results is presented in Table 3, which demonstrates

TABLE 3. COMPARISON OF X-RAY AND CHEMICAL METHODS ON VARIOUS MINERALS

Sample	Thorid, %	
	X-Ray	Chemical
Monazite A	9.7	9.5
Monazite B	6.9	6.5
Monazite C	4.7	4.4
Apatite	0.29	0.19
Magnetic Separate	0.71	0.78
Carbonate	1.02	0.96
Heavy Mineral Separate	2.1	2.2
Siliceous Rock	2.0	2.3
Xenotime	3.3	3.3
Lignite Ash	4.5	4.8
Monazite, Mt. Weather	5.8	5.5
Eschynite	6.6	6.4
Dilute Monazite	0.97	1.00
Black Sand	3.6	3.6
Weathered Vein I	1.80	1.68
Thorianite Ore	1.80	1.87
Weathered Vein II	4.6	4.2

the broad applicability of the x-ray method to a variety of samples.

Columbium and tantalum have been determined in monazite ores using zirconium and hafnium, respectively, as internal standards.¹⁵ The relative precision at the two per cent level of the sought elements is five per cent, and the time of analysis is 40 minutes. Fusion of the sample and co-precipitation with the internal standards are carried out to avoid serious particle size effects.

The purpose in the foregoing discussion has been to point out some of the problems and limitations as well as some of the advantages and achievements of applied x-ray fluorescence. It is the firm belief of many workers in this field that only a beginning has been made in potential applications and that remarkable advances in this technique lie in the years just ahead.

REFERENCES

1. BEATTIE, H. J., AND BRISSEY, R. M., *Anal. Chem.*, **26**, 980 (1954).
2. SHERMAN, J., *Spectrochim. Acta*, **7**, 283 (1955).
3. ADLER, I., AND AXELROD, J. M., *Ibid.*, **7**, 91 (1955).
4. PIRENNE, H. M., "The Diffraction of X-rays and Electrons by Free Molecules," Cambridge University Press, Cambridge, England, 1946.
5. CASTAING, R., AND GUINIER, A., *Anal. Chem.*, **25**, 724 (1953).
6. WALTER, E. R., Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1956.
7. YAO, T. C., *Ibid.*, March, 1958.
8. KEMP, J. W., *Ibid.*, March, 1959.
9. LAMB, F. W., NIEBYLSKI, L. M., AND KIEFER, E. W., *Anal. Chem.*, **27**, 129 (1955).
10. JONES, R. A., Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1959.
11. DAVIS, E. N., AND VAN NORDSTRAND, R. A., *Anal. Chem.*, **26**, 973 (1954).
12. DYROFF, G. V., AND SKIBA, P., *Ibid.*, **26**, 1774 (1954).
13. GUNN, E. L., *Ibid.*, **28**, 1433 (1956).
14. ADLER, I., AND AXELROD, J. M., *Ibid.*, **27**, 1002 (1955).
15. MORTIMORE, D. M., ROMANS, P. A., AND TEWS, J. L., *Appl. Spectroscopy*, **8**, 24 (1954).

E. L. GUNN

GEOMETRY OF X-RAY OPTICS SYSTEMS

In x-ray spectrochemical analysis, single crystals of lithium fluoride, quartz and others are used to disperse the x-ray spectrum in the same manner that ruled diffraction gratings are used to disperse the visible spectrum in ordinary light-emission spectroscopy. Just as in the visible region, scanning spectrometers may be utilized to cover a portion of the x-ray spectrum or fixed x-ray optics may be used to study variations in particular wavelengths of interest. There are three most common geometries for the x-ray optics systems and they are designated according to the way in which the dispersing crystal is used; i.e. flat crystal, curved reflection crystal, and curved transmission crystal. Less common geometries used for special purposes employ doubly curved crystals or ruled diffraction gratings. It is also possible to partially resolve the x-ray spectrum electronically according to the amplitude of the pulse generated in a proportional or scintillation detector (see p. 749). Electronic resolution, if used by itself, is commonly referred to as nondispersive analysis because no dispersing crystal is required.

Flat Crystal Geometry

Fig. 1 shows the simplest arrangement for flat crystal x-ray optics. Primary x-rays of sufficient energy from the x-ray tube excite the characteristic x-ray wavelengths from the elements in the specimen by fluorescence. This fluorescent radiation is emitted in all directions from the specimen and, before dispersion, it is necessary to limit it to a parallel bundle with a collimator. Parallel blades, as shown in the figure, are most commonly used although an array of close-packed tubings gives similar resolution (but lower intensity). Also a single pinhole system or pair of slits could be used but would not increase resolution. For each setting of the crystal one wavelength in the x-ray spectrum will satisfy the Bragg law,

$$n\lambda = 2d \sin \theta, \quad (1)$$

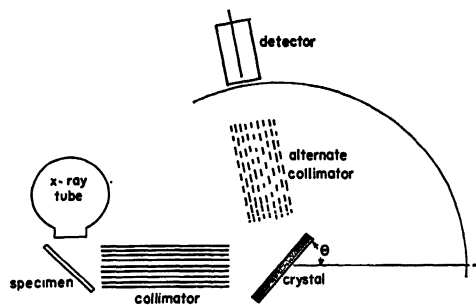


FIG. 1. Flat-crystal x-ray optics. Primary x-rays from the tube excite the characteristic x-ray lines from the elements in the specimen. The polychromatic secondary x-rays are collimated and then diffracted sequentially according to wavelength by the analyzing crystal. A detector measures the relative intensities of the various x-ray lines.

where n is the order (usually 1), λ is the wavelength in Angstrom units ($\text{AU} = 10^{-8} \text{ cm}$), d is the crystal interplanar spacing in AU (2.02 AU for LiF) and θ is the Bragg angle between the incident x-rays and the diffracting planes. By positioning the detector at angle 2θ corresponding to the crystal setting θ , only the diffracted radiation will be detected. As the crystal is rotated through the angle θ from zero to 90° and the detector is rotated simultaneously from zero to 180° the x-ray spectrum is dispersed. There is, however, a limit on the longest wavelength, $\lambda_{\max}$, that may be diffracted by a particular kind of crystal because as θ goes to 90° and $\sin \theta$ goes to unity,

$$\lambda_{\max} = 2d \quad (2)$$

Thus the need for long-spacing crystals is apparent for analyzing the longer wavelength part of the x-ray spectrum.

The d spacing of the crystal also enters into the dispersion $d\theta/d\lambda$. From Bragg's law one obtains

$$d\theta/d\lambda = \frac{1}{2} d \cos \theta \quad (3)$$

Since it is desirable to separate neighboring wavelengths for resolution, $d\theta/d\lambda$ should be large and this means a small value of d is required. The general rule in choosing a

crystal then is: Other things being equal, choose the smallest d spacing possible consistent with being able to diffract the maximum wavelength required (eq. 2). Of course it is better to have a crystal giving a high diffracted intensity than one with slightly shorter d spacing.

Resolution. The resolution of the system depends on the divergence of the collimator, B_C , and the rocking curve breadth, B_M , due to the mosaic structure of the crystal. Fig. 2a shows the Gaussian-type rocking curve that is obtained from good single crystals. For ideally imperfect crystals such as LiF, the breadth at half maximum B_M will be of the order of 0.2° ; for more perfect crystals such as quartz, B_M will be more like 0.05° . Fig. 2b shows the form of the intensity distribution transmitted by a blade collimator. For a collimator 4 inches long with a 0.005-inch blade spacing, the breadth B_C will be about 0.07° . From rules for adding variance, the breadth of a diffracted x-ray line, B , becomes

$$B^2 = B_M^2 + B_C^2 \quad (4)$$

For LiF and the 4 inch collimator mentioned above, B is about 0.21° .

It is possible to place the collimator between the crystal and detector as shown by the dotted lines in Fig. 1 instead of between the specimen and the crystal. Resolution

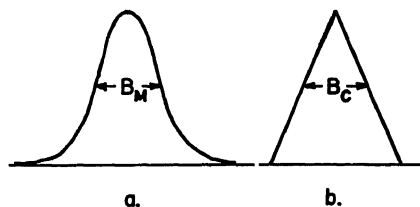


FIG. 2. (a) Normal intensity curve as a function of angle (rocking curve) for a single crystal. The breadth at half maximum, B_M , is due to mosaicity and varies from about 0.05 degree for rather perfect crystals such as quartz to about 0.2 degree for ideally imperfect crystals such as lithium fluoride. (b) Intensity distribution as a function of angle through a blade collimator. For a collimator 4 inches long with blade separation of 0.005 inch, B_C will be about 0.07 degree.

and intensity will be about the same as before but background intensity will be reduced somewhat.

For best resolution, collimators (of equal divergence) should be placed at both positions. With double collimators, the crystal rocking curve has little effect on the resolution and the final breadth may be expressed approximately as

$$B = 0.6 B_0 \quad (5)$$

Of course when two collimators are used, the spectrometer must be more accurately aligned and backlash cannot be tolerated.

Fixed X-ray Optics. Although scanning the x-ray spectrum is the most common practice with flat crystals, it is sometimes feasible to eliminate the spectrometer and just use a fixed crystal and detector in the Bragg condition to monitor a particular x-ray wavelength as in the continuous process control of tin plating.

Another modification of the flat crystal technique is shown in Fig. 3 where the whole spectrum is dispersed without scanning. By using a narrow crystal and/or a limiting blade, the incident and diffracted radiation is confined to a very narrow bundle. From some point on the specimen, radiation of wavelength λ_1 will strike the crystal at the proper Bragg angle and will be diffracted as

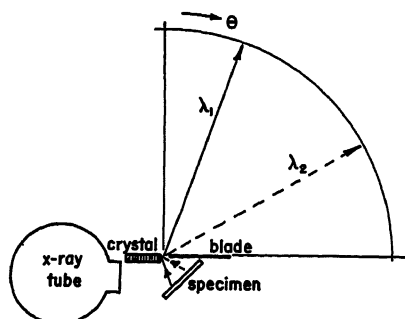


FIG. 3. Edge-type flat-crystal optics. A limiting blade and a narrow crystal combine to limit each diffracted wavelength to a narrow bundle of radiation. No moving parts are required because wavelengths arising from different portions of the specimen are all diffracted simultaneously.

a sharp line. Other wavelengths from other positions on the specimen will likewise be diffracted as shown (the specimen must be homogeneous if quantitative results are to be obtained). The whole spectrum may be recorded on photographic film in about the same length of time it takes with a scanning spectrometer, and resolution may be made comparable. If only a few lines are to be measured, then the scanning spectrometers are faster, because for each line the diffracted intensity per unit time is much higher with the large crystal.

Crystal Treatment. The effects of analyzing crystal treatment for best diffraction is treated in detail in Birks' book. Generally with the alkali halides, introducing additional dislocations in the crystal by abraiding or stress will increase the diffracted intensity by as much as ten times over that from cleavage surfaces and without serious loss of resolution.

Curved Reflection Crystal Geometry

Fig. 4a shows the geometry of curved reflection x-ray optics. If a circle of radius R is established (the Rowland circle in light optics), x-rays diverging from a point or line source on that circle may be diffracted from a properly curved crystal and the diffracted radiation will converge to a line image on the focusing circle. For each setting of the crystal along the circle, only one wavelength will satisfy the Bragg condition and be diffracted. As shown in Fig. 4a, primary radiation from the x-ray tube again excites the characteristic wavelengths of the specimen elements. A slit close by the specimen and located on the focusing circle acts as the required line source of diverging radiation.

For the best resolution the crystal is first curved to a radius $2R$ equal to the diameter of the focusing circle and then the surface is ground to the radius of the focusing circle. The rocking curve breadth of the curved crystal should remain approximately the same as that of the flat crystal, provided

reasonable care is exercised in curving and grinding. The angular divergence corresponding to that of the collimator in flat crystal optics is controlled by the source-slit width. For an 8-inch (20 cm) radius focusing circle a slit width of about 0.015 inch will correspond in divergence to the 4-inch long 0.005-inch spacing collimator. A second slit ahead of the detector acts in the same way as the second collimator for flat crystal optics.

A useful variation of the curved-crystal optics for inhomogeneous specimens is shown in Fig. 4b where the flat specimen is mounted so as to intersect the focusing circle. The primary radiation is masked with a lead pinhole so that the only part of the specimen irradiated is a circle about 0.5 mm in diameter at the intersection with the focusing circle. By translating the specimen, different areas are brought to that position, thus the composition variation across the surface is easily obtained.

Another interesting variation with curved-crystal optics is shown in Fig. 4c where the specimen is in the form of a fine rod or wire mounted on the focusing circle. A specimen of very small total mass may be examined in this way. For instance, about 1 milligram in the form of a wire will yield intensity comparable to a flat specimen of several grams mounted as in Fig. 4a.

Carrying this idea one step further to the very minimum quantity in grams that will give a measurable intensity, the curved crystal arrangement should be about 100 times more sensitive than flat crystal optics. This is based on comparing curved LiF with a 0.015-inch source slit and flat LiF with a 4-inch long, 0.005-inch spacing collimator. The factor of 100 comes about because in flat-crystal optics, radiation from any atom in the specimen is limited by the collimator and can reach only a strip about 0.010 inches wide on the crystal whereas it can reach the whole crystal in curved-crystal optics. Even for a 1-inch crystal this is a factor of 100

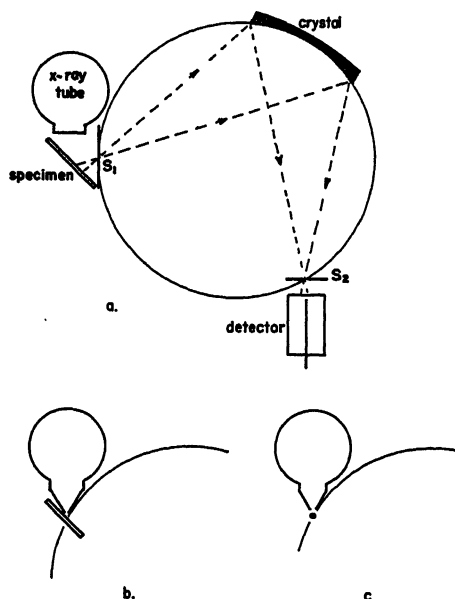


FIG. 4. Curved-crystal reflection x-ray optics. (a) Excitation of the characteristic wavelengths is the same as for flat-crystal optics but a limiting slit on the focusing circle acts as a divergent line source of radiation. For each setting of the crystal, one wavelength only is diffracted and the radiation converges to a line image on the focusing circle. (b) A pinhole limits primary radiation to a circle about 0.5 mm so that only a small area of the specimen surface is irradiated. By mounting the specimen properly, this irradiated area may be located on the focusing circle where it acts as a divergent point source of radiation. As the specimen is translated past the primary beam, different areas are excited, and any inhomogeneities are indicated by variation of the intensities of the characteristic lines. (c) A wire or capillary type specimen may be mounted on the focusing circle and acts as a divergent line source of radiation. Very small total volumes of material may be examined by this method.

times. In practice it is not easy to attain the theoretical increase of 100 times, probably because the specimen is not mounted exactly on the focusing circle, the crystal does not have strictly uniform curvature, or the specimen contains too much material and there is some self-absorption when mounted in capillary form. Factors of about 10 times have been reported by several workers.

Curved Transmission Crystal Geometry

Curved-crystal transmission optics is somewhat different in principle than curved-crystal reflection optics. It should be noted that this is not the same as in flat-crystal optics where transmission is a trivial modification of reflection. Figs. 5a and b show the two possible situations. Again the crystal is curved to a radius equal to the diameter of the focusing circle, but grinding the surfaces to the radius of the focusing circle is far less important than in reflection optics. The correct thickness of the crystal is quite critical and varies with wavelength because of the rapidly changing absorption coefficient for the characteristic lines of interest. The proper thickness is such that ratio of transmitted to incident radiation $I_T/I_0 = 1/e$ for the wavelength of interest and e is the base for natural logarithms.

In Fig. 5a a flat specimen on the convex side of the crystal is excited by primary radiation in the usual manner. The various wavelengths are diffracted by the planes perpendicular to the crystal surface and the diffracted radiation converges along the focusing circle. No motion of the crystal is

necessary but the detector has to move along the circle to measure the various wavelengths.

In Fig. 5b a rod or wire specimen is mounted on the focusing circle on the convex side of the crystal. With the crystal at position A, some wavelength λ_1 will satisfy the Bragg law and be diffracted. The diffracted radiation will continue to diverge, however, unlike the reflection situation in Fig. 4c. At position B in Fig. 5b the crystal will selectively diffract a different wavelength λ_2 , and so on, until the whole spectrum is dispersed.

Some intensity is inevitably lost by absorption in curved transmission optics. But for short wavelength radiation, the solid angle of radiation intercepted from a point source is so much larger than for reflection optics that the total diffracted intensity is often appreciably higher.

Doubly-Curved Reflection Crystals

For some special x-ray problems it is desirable to diffract a particular wavelength from a point source to a point image. This is possible with a doubly-curved crystal prepared for the particular desired wavelength.

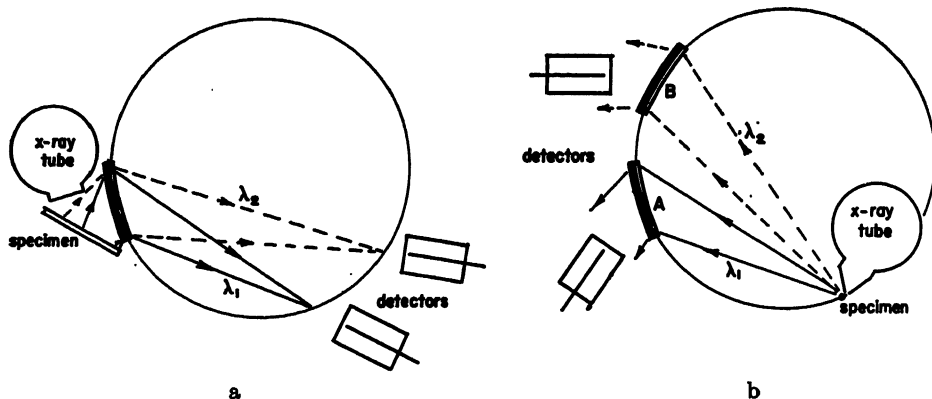


FIG. 5. Curved-crystal transmission x-ray optics. (a) A large specimen outside the focusing circle may be excited in the same manner as in flat-crystal optics. Different wavelengths will be diffracted and converge along the focusing circle with the crystal stationary. Fixed detectors or a moving detector may be used to measure the intensity. (b) A wire or point specimen may be mounted on the focusing circle and acts as divergent source of radiation. For each position of the crystal only one wavelength is diffracted; the diffracted radiation continues to diverge after passing through the crystal. Either fixed or moving detectors may be used.

Such procedure is quite reasonable in x-ray diffraction where the same characteristic radiation from the x-ray tube target is to be used over and over. It is not so reasonable for x-ray spectrochemical analysis because a doubly-curved crystal is suitable for only one element and only in fixed rather than scanning optics. The requirements on the crystal may be understood by referring back to Fig. 4a. If a line is drawn from the source slit S_1 to the detector slit S_2 , the crystal planes must be warped to fit the figure of revolution formed by rotating the arc of the focusing circle about the axis S_1S_2 . Crystals of LiF, aluminum and perhaps others have been prepared in the doubly-curved form but it takes a rather skillful technique. The double curvature may be approximated by using thin strips of singly curved (and ground) crystals and cementing them on a form with the proper second curvature.

Ruled Gratings

In the very beginning days of x-rays, attempts were made to use ruled gratings for diffraction as in classical optics. It was soon discovered that the x-rays were reflected only at grazing incidence and that even the finest rulings of 20 to 30 thousand lines per inch (spacings of 6-8000 AU) were far too coarse for the 1 to 10 AU range of x-rays. Therefore workers turned to three dimensional single crystals having spacings of 1 to 10 AU to diffract the radiation. With the recent success of x-ray spectrochemical analysis in the 1 to 10 AU range there has been increasing interest in pushing the technique to the 10 to 100 AU range. This would cover the characteristic lines of the light elements such as carbon, nitrogen, and oxygen and would also cover a most interesting region in the solar and stellar x-ray spectrum. The difficulty is that crystals do not have sufficiently long interplanar spacings to diffract such wavelengths and it is necessary to turn back again to ruled diffraction gratings. The geometry with ruled gratings is very much like that of

Fig. 4a except that the radius of curvature of the focusing circle is of the order of 100 cm instead of 10 to 20 cm and the diffraction angles are limited to the order of 5° or less. The principle of diffraction with ruled gratings is not quite the same as with crystals, however, and the equation for diffraction is expressed as

$$\lambda D = (\cos \varphi_1 - \cos \varphi_2) \quad (6)$$

where λ is again the wavelength, D is the ruling spacing, φ_1 is the angle between the incident radiation and the grating surface, φ_2 is the angle between the diffracted radiation and the surface. Unlike crystal diffraction, the incident and diffracted angles are not necessarily equal. Also, the whole spectrum is diffracted without turning the grating.

It is expected that the use of ruled gratings will increase rapidly as the long wavelength x-ray spectrum is exploited.

Useful Relations

Bragg diffraction law for crystals

$$n\lambda = 2d \sin \theta$$

where λ is wavelength in AU; d is interplanar spacing in AU; θ is Bragg angle (the angle between the incident radiation and the diffracting planes)

Dispersion

$$\frac{d\theta}{d\lambda} = \frac{1}{2d \cos \theta}$$

It is of advantage to use a crystal with the smallest d value feasible because the dispersion is greater.

Maximum wavelength diffracted for a given crystal

$$\lambda_{\max} = 2d$$

Diffraction equation for ruled grating

$$\lambda = D(\cos \varphi_1 - \cos \varphi_2)$$

D is distance between rulings (8.33×10^{-5} cm for a grating containing 30000 lines/inch)

φ_1 is the incident angle corresponding to θ for crystal diffraction

φ_2 is the diffracted angle but is no longer equal to φ_1 as in crystal diffraction.

L. S. BIRKS

SCANNING MICROANALYZER

The technique of focusing an electron beam to produce a high intensity point source of x-rays has been discussed by Nixon (Enc. of Microscopy, "Point Projection X-Ray Microscopy"). It was early realized that the x-ray projection microscope could be used for the chemical analysis of a selected region in a specimen down to $1\text{--}10\mu$ in extent, by study of its x-ray absorption or fluorescence spectra. Independently of Cosslett and Nixon, an instrument was developed by Castaing^{1, 2} for microanalysis by directly excited x-ray emission, in which the specimen itself is bombarded by a beam of electrons focused into a probe about 1μ in diameter. In combination with a technique for scanning the electron probe over the specimen surface, which is the subject of this article, the method can be used to obtain the surface distribution of a given element in the form of a visual image. The x-ray scanning micro-analyzer is thus of value in investigating surface inhomogeneity, and has been widely applied to problems in metallurgy and mineralogy.

To introduce the principles underlying the x-ray scanning microanalyzer it is first necessary to consider the emission method of microanalysis using a stationary electron probe. Following the work of Castaing, several types of static probe microanalyzer have been developed, nearly all employing a two-

lens system to give a probe of diameter $1\text{--}5\mu$; the accelerating voltage is commonly between 20 and 40 kV. Designs of the objective lens, specimen chamber and spectrometer have differed considerably, but all rely on being able to position the electron probe on the specimen surface by means of an optical microscope accurately aligned with the electron-optical axis. One or more crystal spectrometers are then used to analyze the characteristic x-rays emitted from the selected point on the surface.

A typical emission spectrum plotted with a lithium fluoride crystal spectrometer is shown in Figure 1. This was excited from a volume of about $1\mu^3$ in a piece of ferrite material, and illustrates how the elements present may be identified from the Bragg angles or wavelengths of the characteristic peaks; in this case the $K\alpha$ and $K\beta$ peaks of Mn, Fe and Zn are visible. The concentration of each element may then be determined from the peak height, to which it is approximately proportional, calibration being effected by comparison with a pure sample of each element or with a standard of known composition. A relative accuracy of 1 % in the determination of high concentrations is possible in favorable cases, with a minimum detectable concentration of less than 0.1 %. Owing to the experimental difficulties of dispersing and detecting x-rays of wavelengths longer than a few Angstrom units without considerable loss of intensity, the method cannot at present be easily applied to elements lighter than magnesium ($Z = 12$, $Mg K\alpha = 9.9\text{\AA}$). However, present work is directed towards extending this limit, as referred to later in this article.

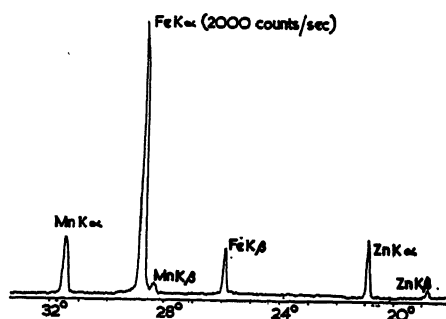


FIG. 1. X-ray emission spectrum from manganese-zinc ferrite, plotted with a curved crystal of lithium fluoride.

Principle of the Scanning Microanalyzer

The principle of the x-ray scanning microanalyzer may be described with reference to Figure 2, which shows the original instrument of Cosslett and Duncumb.³⁻⁵ The electron probe, 1μ in diameter, is focused by two magnetic lenses on to the specimen at the

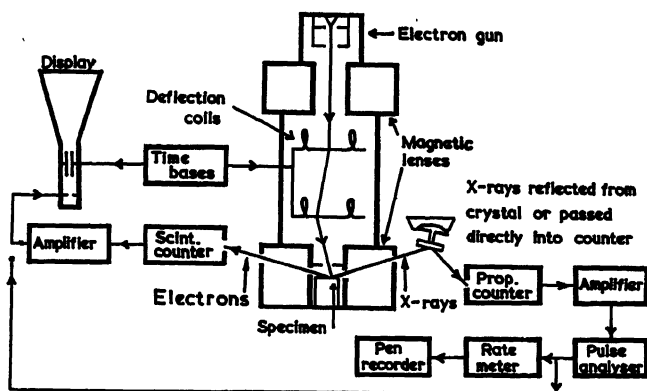


FIG. 2. Block diagram of the x-ray scanning microanalyzer.

bottom of the column, and is scanned over the surface by deflection coils between the lenses. X-rays emerge through a port on the right of the objective lens, and characteristic radiation of a particular wavelength may be selected either with a crystal spectrometer or with a proportional counter and pulse analyzer. The amplified signal modulates the beam of a cathode ray tube scanned in synchronism with the probe, which thus displays the surface distribution of the corresponding element. Alternatively, with the scintillation counter on the left, back-scattered electrons may be collected to form an image of the surface topography of the same area, in a fashion somewhat similar to the scanning electron microscope of Smith and Oatley.⁷ The scanning rate is 1 frame in about 2 sec. and the image is built up in the display screen afterglow, which persists for about 20 sec. The maximum area of scan is at present limited to $400\mu \times 400\mu$, owing to off-axis aberrations of the objective lens.

After an electron or x-ray image has been obtained, the scan may be stopped and the electron probe accurately located on a particular feature in the surface by adjusting the position of the display tube spot on the retained image. Quantitative analysis may then be carried out in the same way as with the static probe instrument.

One further feature of the instrument is its ability to display semiquantitatively the

distribution of an element along a given line in the specimen. With the appropriate radiation selected, the electron probe is set to scan slowly along this line in a period of five seconds or more and the output of the rate-meter is used to produce a Y deflection on the display tube, which is scanned in the X direction in synchronism with the probe. It is convenient in practice to have two identical display tubes, one of which is used for this purpose and the other to position the line from the x-ray or electron image.

Thus the main advantages of the scanning technique are the following. The distribution of a particular element can be obtained much more rapidly than in a point-by-point analysis using a static electron probe. Secondly, the accuracy of focusing and locating the electron probe is not limited by the resolution of an optical microscope, and errors due to interaction of stray lens field with a ferromagnetic specimen are eliminated.

Theoretical Considerations

The theory governing the design and use of the x-ray scanning microanalyzer, as with other instruments of this type, is mainly concerned with a balance between resolution and x-ray intensity. The resolution may be taken as the diameter of the x-ray source, which is dependent on three main factors:

(1) The geometrical diameter of the electron probe, as determined by the electron-

X-RAY EMISSION SPECTROMETRY

optical demagnification and by the effective size of the electron source in the gun:

(2) The spreading of the probe due to spherical aberration of the objective lens:

(3) The penetration and lateral scattering of the incident electrons within the specimen.

In principle each of these can be reduced to any desired level by increasing the demagnification, reducing the lens aperture or reducing the accelerating voltage, respectively, but only at the expense of x-ray intensity. It is therefore necessary to fix the minimum x-ray intensity required and to combine these three factors in such a way as to give the minimum over-all diameter to the x-ray source, that is, to give the best resolution. This problem has been considered theoretically by Wittry,⁸ and with particular reference to the scanning microanalyzer by Duncumb.⁶

The minimum x-ray intensity required is set by statistical considerations. The effect of

a low x-ray intensity on the image is to give it a grainy or noisy appearance, due to random fluctuation of the number of quanta representing any one image point. To obtain the maximum amount of information from the image, the x-ray intensity should be sufficiently high that these fluctuations are invisible. However, this would require a counting rate in the region of 10^7 /sec, which no system can at present handle, and it is therefore necessary to accept a certain amount of noise in the image. Figure 3 illustrates the progressive increase of noise in the image as the count rate is reduced. The specimen was a 200-mesh/inch copper grid; Cu $K\alpha$ radiation was selected with the crystal monochromator so that the superimposed silver grid appears dark. At the lowest count rate of 500 counts/sec, which is about 20,000 times lower than the rate for a noise-free image, the form of the copper grid is plainly visible, though little can be said about detail in the surface. In practice a count rate of

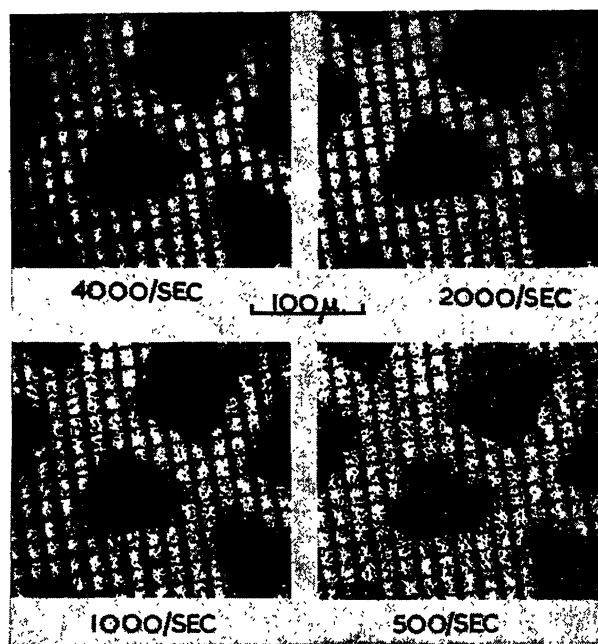


Fig. 3. X-ray scanning image, with Cu $K\alpha$ radiation selected, of 200 mesh/in. copper grid and superimposed silver grid, showing increase in graininess as count rate is reduced. Exposure 2 min.

10^3 – 10^4 /sec is sufficient for many purposes. Improvement in quality is given by recording the image photographically for a period of several minutes; alternatively, when interest is confined to a particular feature in the image, the area of scan can be reduced to cover a smaller number of lines, so that the available quanta correspond to fewer image points.

Having fixed the x-ray intensity required, it is then possible to estimate the best resolution attainable. If the three factors mentioned above which contribute to the x-ray source diameter are combined in optimum proportions, simple theory indicates that the count rate n for a given characteristic line should vary roughly as the fourth power of the x-ray source diameter d , i.e., the resolution. The constant of proportionality can be split into three parts k_s , k_o and k_e , relating to the electron-optical system, the efficiency of x-ray production in the specimen, and the efficiency of the x-ray spectrometer.

That is,

$$n = k_s k_o k_e d^4 \quad (1)$$

If typical values for these constants are inserted, assuming the normal type of electron gun, magnetic lenses and crystal spectrometer, the best resolution that can be expected for a specimen of pure copper, with a count rate of 10^4 /sec, is about 1μ . The optimum accelerating voltage should then be about 17 kV and the probe current $1\mu\text{A}$. Such a performance can be realized in practice, though it is convenient where possible to work under somewhat relaxed conditions with an accelerating voltage of about 25 kV and a correspondingly lower probe current. For specimens other than copper, the optimum accelerating voltage will take a different value depending on the threshold excitation voltage. It is noteworthy that if the required counting rate is fixed, the dependence on the fourth power of d means that a substantial reduction in d can only be achieved through a large increase in k_s , k_o ,

or k_e ; this point will be considered further later.

Design of the Electron-optical System

As with the static probe instrument, the design of the electron-optical system centers around the inter-relation of the objective lens, x-ray spectrometer and specimen mounting facilities.

The main features desirable are:

- (1) an objective lens of short focal length for low spherical aberration;
- (2) space for large specimens and ease of interchange;
- (3) the specimen surface normal or near normal to the electron-optical axis to avoid defocusing at maximum probe deflection;
- (4) the x-rays collected at a high angle to the surface to reduce absorption of the emergent beam.

The relative weights put on these features have caused existing designs to differ widely, depending on what the equipment is required to do. In mineralogical work, for example, the need to be able to examine rough surfaces with a high emergent angle overrules the desirability of a short focal length lens. The high probe current which this would permit cannot in any case be used, owing to the low thermal conductivity of most minerals. On the other hand, to detect trace elements present in a polished metal specimen, the high probe current required may swing the balance the other way. It thus seems unlikely at present that one design will satisfy all applications.

In the first instrument developed by Cosslett and Duncumb,³⁻⁶ the specimen was accommodated in the bore of the polepiece and x-rays were collected through the polepiece gap, as Figure 2 indicates. It was found, however, that for most applications, more than sufficient probe current was available, indicating that a longer focal length lens would be practicable. Thus, in a second instrument constructed by Duncumb and Melford⁹ at Tube Investments Research

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Laboratories, the major disadvantage of this arrangement—the restricted size and the difficulty of interchange of the specimen—was removed by incorporating a lens of the pinhole type with the focus outside the polepiece.

A sectional diagram of the column of this instrument is shown in Figure 4. Two lenses are used to focus the probe on to the specimen immediately beneath the second lens, in the upper bore of which deflection coils are mounted to scan the probe over the specimen surface. Emitted x-rays and scattered electrons are collected at 20° to the specimen surface through ports in the lens casing in a plane perpendicular to that of the diagram. The specimen is mounted on a horizontal table, and may be traversed or rotated about the optical axis or moved from under

the electron beam to an optical microscope or airlock. Several other positions on the table accommodate standard samples. A complete view of the instrument is given in Figure 5, showing the column and control desk on the left, the scanning and counting racks in the middle and pen recorder on the right. This instrument is now manufactured commercially.

For mineralogical work Long¹⁰ has described the use of a scanning microanalyzer in which the probe is focused nearly 2 cm outside the lens to give space for a rock section mounted on a standard glass slide. This is held at 45° to the electron-optical axis so that x-rays can be collected at a high angle to the surface, which may be observed during analysis either in transmitted or reflected light. Optical fluorescence at the point of impact is often visible and gives additional qualitative information. Electrostatic scanning plates are located between lens and specimen. Also using electrostatic deflection, Mulvey¹¹ has added a simple scanning system to his static probe instrument, the plates in this case being located in the polepiece gap.

Applications

The type of information that can be obtained with the x-ray scanning microanalyzer is illustrated in Figure 6. The specimen is an alloy of iron with copper, nickel and tin, in which an iron-rich phase has crystallized in the form of dendrites. These are shown in the optical image (a) of a polished section of the material, and in (b), the electron scanning image of the same field. The presence of iron in the dendrites is confirmed in (c), which was obtained by selecting Fe $K\alpha$ radiation with the crystal spectrometer. Part of this image is shown at higher magnification in (d), together with a plot of the distribution of iron, photographed from the second display tube as the electron probe was scanned slowly along the line shown. Qualitative and semiquantitative information

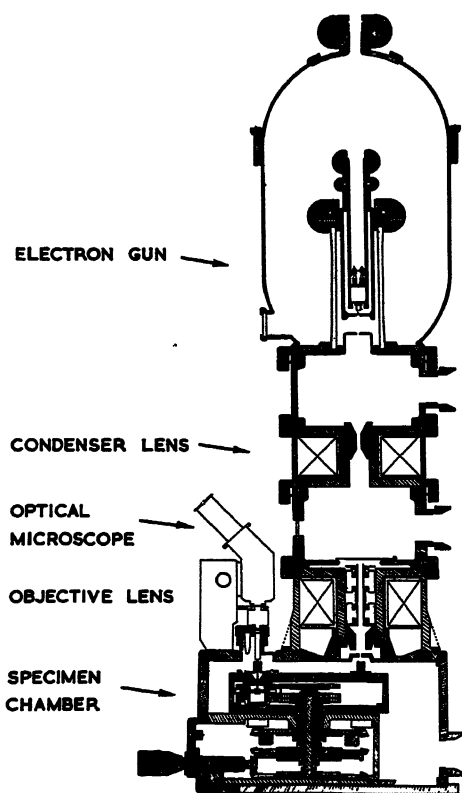


FIG. 4. Electron-optical system of x-ray scanning microanalyzer.



FIG. 5. Complete x-ray scanning microanalyzer.

about the surface distribution of an element can thus be obtained, which is of particular value when the segregation is not visible optically, as in the case of some solid solution effects. The next step in a detailed investigation would be quantitative analysis at selected points of interest revealed by such a study.

Another important advantage of the scanning microanalyzer is that of accurate location of the electron probe on a selected feature. Since this is carried out by reference to a magnified image obtained by means of the probe itself, an accuracy of better than the probe diameter is attainable. This is shown particularly in a study of carbide particles on a carbon film extraction replica. In this case, the particles may be well below 1μ in size, so that a large fraction of the incident electrons is transmitted, and the effect of lateral diffusion is reduced. A smaller x-ray source can then be obtained and the resolution of the microanalyzer is correspondingly improved. Figure 7(a) shows the electron scanning image of carbide particles

extracted from a steel surface, and Figure 7(b) is the x-ray emission spectrum plotted from a selected particle A, which is seen to contain chromium and manganese. The diameter of A is found from the normal electron micrograph of the same field (Figure 7(c)) to be about $3000\text{\AA}$. It is thus possible to analyze, at least qualitatively, individual particles on or below the limit of resolving power of the optical microscope, and a wide range of applications in conjunction with the electron microscope is foreseen.

Other applications have included studies of segregation and nonmetallic inclusions in steel,^{12, 13} manganese distribution in three-phase aluminium-bronze,¹² fracture surface precipitates in beryllium,¹² crystallization in copper-bismuth alloy,¹¹ ex-solution intergrowth in natural minerals,¹⁰ and tin oxide particles in human lung section.

Conclusions

The x-ray scanning microanalyzer has already proved a useful tool for the analysis of regions down to 1μ in size and of elements

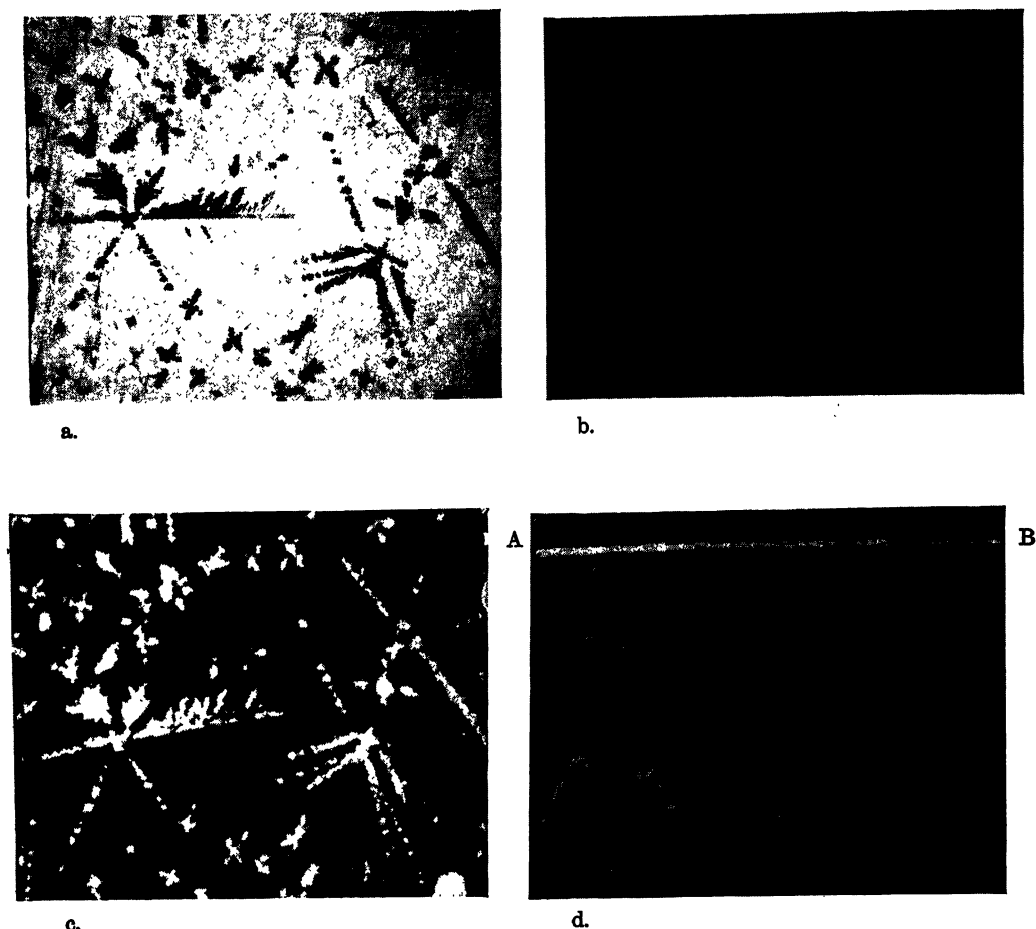


FIG. 6. Iron rich dendrites in Fe-Cu-Ni-Sn alloy. (a) Optical image. (b) Electron scanning image. (c) X-ray scanning image selecting Fe $K\alpha$ radiation. (d) Distribution of iron along line AB intersecting dendrite.

down to 12 in atomic number. Present work is directed towards improving both these limits, which have in common the need for using a lower accelerating voltage than the normal 20–40 kV; the reduced electron penetration improves the resolution in a thick specimen and cuts down the strong absorption which the long-wavelength characteristic emission of light elements undergoes on leaving the specimen.

To maintain sufficient x-ray intensity with improved resolution, some way must thus be found of materially increasing k_a , k_o , or k_s in equation 1, as noted previously. The greatest

room for improvement lies in the factor k_s , representing the efficiency of the x-ray detecting system; present curved crystal spectrometers make use of only about 10^{-5} of the total emitted radiation. With a proportional counter mounted close to the specimen, k_s can be increased by as much as 10^4 times, which indicates a possible improvement of resolution from 1μ to 0.1μ . The disadvantage of spectrometry by means of a proportional counter and pulse height analyzer is that the wavelength resolution is comparatively poor; the K radiations from elements closer than about 3 in atomic number are not directly

resolved. However, a proportional counter may be used where the characteristic radiations are sufficiently far apart, and a resolution of 0.3μ has already been demonstrated in an aluminum-tin specimen, using a voltage of 6 kV. It seems likely that 0.1μ will eventually be obtained in a specially designed system suitable for accelerating voltages in this region.

With regard to the extension of the detection system to wavelengths longer than $10\text{\AA}$ for the purpose of analyzing elements lighter than magnesium, it seems that the solution may again be provided by the use of a proportional counter. It is possible to use a diffraction grating with detection by an electron multiplier, but the efficiency of this arrangement is very low, precluding its use in a scanning system. For this reason, Dolby,^{14, 15} has approached the problem by applying special methods of pulse analysis to the proportional counter to effectively improve the wavelength resolution. One method has been successfully used to obtain separate scanning images of Mg, Al and Si present in one specimen. There seems no reason why this should not be applied to C, N and O, elements of particular interest to the metallurgist and biologist alike, once a suitably thin window for the counter, transparent to these long wavelengths, has been found.

Commercially available 6μ "Mylar" forms too thick a window for the efficient detection of nitrogen and oxygen, but the filtering action of this carbon-rich material renders it usable in the detection of $44\text{\AA}$ carbon K radiation.¹⁵ Scanning images of graphite flasks in cast iron have been obtained in this way.¹² For nitrogen and oxygen, a thinner film of collodion, or some similar material which can be cast on water, appears the most promising, though difficulties in mounting and supporting it on a mesh at present make it a less reliable vacuum wall. It is likely, however, that these technical difficulties will soon be overcome.

Prospects for improving both the resolving

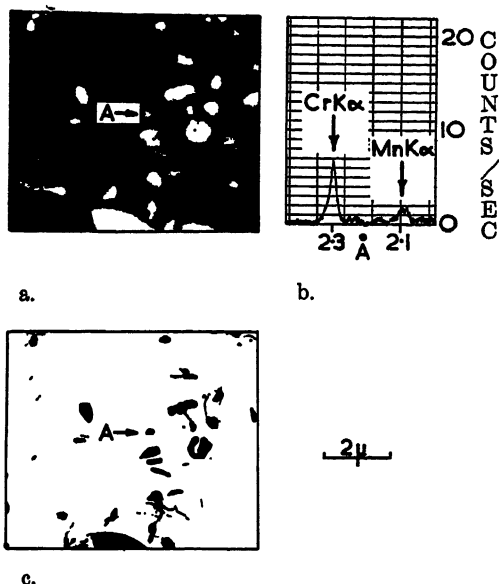


FIG. 7. Carbide particles in extraction replica from steel. (a) Electron scanning image. (b) X-ray spectrum from particle A. (c) Normal electron micrograph showing A to be about $3000\text{\AA}$ diameter.

power and the range of the x-ray scanning microanalyzer are thus good. However, possible applications have as yet been only superficially investigated, and much work remains to be done within the present limitations of the method.

REFERENCES

1. CASTAING, R., Thesis, Paris University, O.N.E.R.A. Publ. No. 55 (1951).
2. CASTAING, R., AND DESCAMPS, J., *La Recherche Aeronautique*, **63**, 41 (1958).
3. COSSLETT, V. E., AND DUNCUMB, P., *Nature*, **177**, 1172 (1956).
4. DUNCUMB, P., AND COSSLETT, V. E., Proc. Symp. X-ray Microscopy and Microradiography, Cambridge 1956, p. 374, Academic Press, New York, 1957.
5. DUNCUMB, P., Ref. 4. p. 617.
6. DUNCUMB, P., *Brit. J. Appl. Phys.*, **10**, 420 (1959).
7. SMITH, K. C. A., AND OATLEY, C. W., *Brit. J. Appl. Phys.*, **6**, 391 (1955).
8. WITTEY, D. B., *J. Appl. Phys.*, **29**, 1543 (1958).
9. DUNCUMB, P., AND MELFORD, D. A. Proc. Symp. X-ray Microscopy and Microanalysis, Stockholm, 1959. paper 52 (In press.).

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10. AGRELL, S. O., AND LONG, J. V. P., Ref. 9, paper 57.
11. BERNARD, A., BRYSON-HAYNES, D., AND MULVEY, T., *J. Sci. Instr.*, **36**, 438 (1959).
12. MELFORD, D. A., AND DUNCUMB, P., *Metalurgia*, **61**, 205 (1960).
13. MELFORD, D. A., Ref. 9, No. 59.
14. DOLBY, R. M., *Proc. Phys. Soc.*, **73**, 81 (1959).
15. DOLBY, R. M., AND COSSLETT, V. E., Ref. 9, No. 51.

P. DUNCUMB

SOLAR X-RAYS

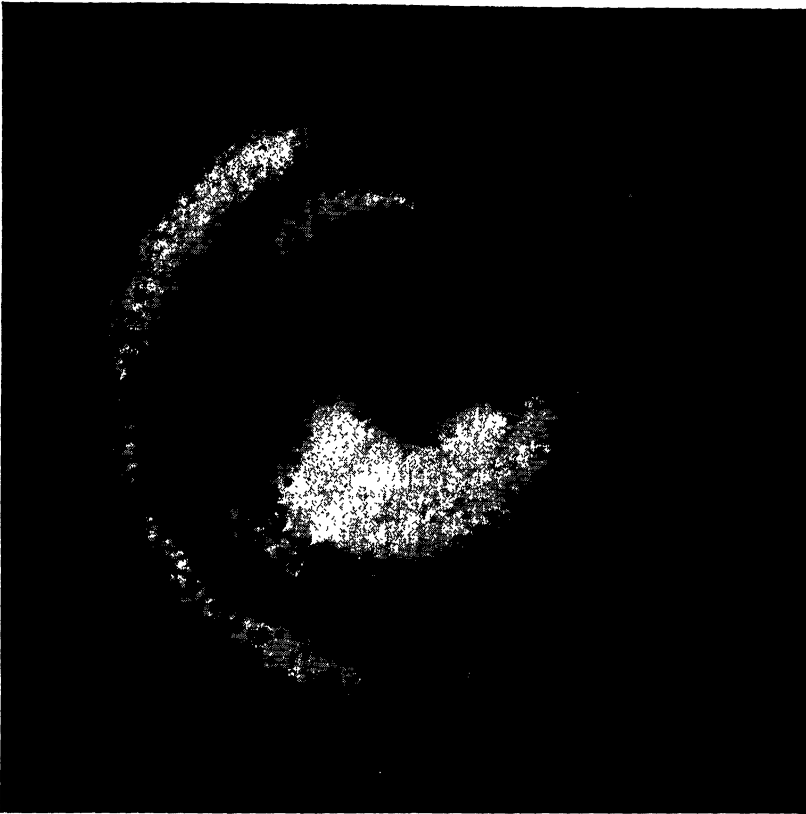
Scientists of the Naval Research Laboratory succeeded late in April 1960 in obtaining the first x-ray photograph of the sun, using an Aerobee-Hi rocket to carry the camera above the atmosphere. The sun's x-rays do not penetrate the air below a height of 60 miles. The photograph shows the sun rimmed by a bright x-ray halo with several intense spots of bright x-ray emission distributed over the disk. The significance of the photograph was explained to the Symposium on Solar Emissions and the Interplanetary Medium of the National Academy of Sciences and the American Geophysical Union, April 28, 1960 at Washington, D. C. by Dr. Herbert Friedman, Superintendent of the Atmosphere and Astrophysics Division of the U. S. Naval Research Laboratory.

The visible disk of the sun is characterized by a surface temperature of 6000° K. Extending high above the disk is the thin outer atmosphere of the sun—its corona. Because its brightness is only one millionth that of the disk—roughly equal to the full moon—the corona can be seen only during a total eclipse, at which time it appears to stretch millions of miles into space. The coronal gas is very tenuous but very hot, the average temperature being about a million degrees with local hot spots reaching perhaps ten million degrees. At this very high temperature the gas is completely ionized, and the electrons race about at such high speeds that

their collisions with the heavy nuclei generate x-rays. The x-ray intensity has been measured from rockets and has been found to play an important role in the formation of the ionosphere, which in turn controls long-range radio communication.

The accompanying photograph is the first ever made of the sun in its x-ray emission. The experiment, prepared by Ensign Richard L. Blake and Mr. Arlyn E. Unzicker of the Naval Research Laboratory, was flown in an Aerobee-Hi rocket from White Sands Missile Range on April 19 at 7:30 a.m., local time. To recover the camera, the instrumentation section was separated from the rocket before impact and parachuted to the ground. Because x-rays cannot be focused by lenses or mirrors in the manner of visible or ultraviolet light, a simple pinhole camera was used. Every school boy has at sometime or other poked a pinhole in one end of a shoe box, cut a square patch out of the other end of the box, and covered it with tissue paper to make a pinhole camera. The image on the tissue paper appears inverted and its size is proportional to the length of the box. The finer the pinhole, the sharper the image.

For the x-ray camera, the pinhole was five thousandths of an inch in diameter and the camera was six inches long. The pinhole was covered by a thin plastic film supporting an opaque coating of aluminum. In this way visible light was blocked but x-rays were passed. The wavelengths effectively transmitted were in the range 20 to 60Å. Because the sun subtends an angle to one-half degree, the image on the film at the back end of the camera was only one-twentieth of an inch in diameter. The accompanying photograph is a direct enlargement of the original film. During the rocket flight to 130 miles above the White Sands Missile Range, the pinhole camera was mounted on a biaxial pointing control which aimed the camera at the sun throughout the flight. Although the



(Official U. S. Navy Photograph)

FIG. 1. X-ray photograph of the sun made by Ensign Richard L. Blake, USN and Mr. Arlyn E. Unzicker, U. S. Naval Research Laboratory. Photograph was obtained from an Aerobee-Hi rocket launched from the Naval Missile Test Facility at White Sands Missile Range, April 19, 1960.

pointing was accurate to one-half minute of arc or one-sixtieth of the solar diameter, the rocket's motion caused the camera to turn slowly about its axis as the flight progressed. Thus any details in the photograph were smeared through concentric arcs of about 150 degrees. The smearing, however, did not obliterate the most interesting features of the photograph.

According to Dr. Friedman, the bright ring around the periphery of the disk represents the thickness of the coronal atmosphere from which the x-rays are emitted. Because this shell of gas is completely transparent to its x-ray emission, it looks dimmest near the center where the emitting region in the line

of sight is thinnest. Looking edgewise through the shell, the thickness is much greater and the rim appears correspondingly brighter. Virtually all of the x-ray emission is confined to a height of about one-fifth of a solar radius above the disk.

At the time of flight, a bright visible plage of calcium light appeared near the center of the disk, just below the equator. The same region seems to be responsible for a brilliant x-ray emission. In spite of the smearing resulting from the camera rotation, there is clear evidence that most of the x-ray emission originates in a few localized areas of the corona.

(From an official news release.)

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X-RAY TELESCOPE FOR THE 1-100 Å REGION

The recent pinhole radiograph of the sun made by Friedman [1960] clearly points up the need for image-forming devices to focus on solar and other x-ray sources in space. In the wavelength region from about 100 Å to 1000 Å the zone plate described by Baez [1960] should work well for intense sources. But the zone plate is a highly chromatic device and therefore it is limited to the study of sources that emit line spectra or radiation that can be monochromatized. There is need for achromatic image-forming devices that are faster than the zone plate and can operate in the shorter wavelength region from about 1 Å to 100 Å. Two such devices are described below. A crude prototype of the first has been built and has made the pictures shown in Figures 1 and 2. The second device is a contemplated refinement of the first for which components are being designed and constructed.

The first telescope consists of two thin, plane, glass mirrors each approximately 1

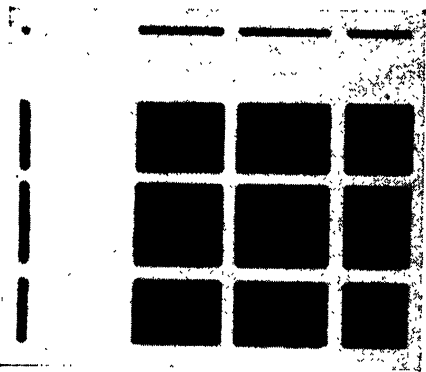


FIG. 1. The image of a small hole illuminated by 2537 Å radiation made by the plane mirror multiple crossed-mirror system. The large area with thin white lines through it was produced by the direct beam. Above this is the exposed region produced by the rays that were reflected only by the first set of mirrors. To the left of the direct beam is the region produced by rays that were reflected only by the second set of mirrors. In the upper left hand corner is the image of the source. It was formed by light reflected from both sets of mirrors.



FIG. 2. To show that a multiple crossed-mirror system is capable of producing an image of an extended object, an opening in the shape of a question mark was illuminated, by transmission, with white light. Its image appears in the upper left. The other regions represent the direct beam, and the beams that experienced reflection at only one of the two mirror arrays as explained in Fig. 1.

in. x 3 in. disposed like the shades of a venetian blind, followed by an identical array at right angles to the first. The effect of the first set alone would be to take x-rays from a point source at infinity and focus them on a line whose width is determined, to a first approximation, by the product of the mirror width and the sine of the grazing angle of incidence. The long edges of the mirrors are parallel but the normals to the reflecting surfaces make slightly different angles with the incident beam so that all reflected beams coincide in a chosen focal plane normal to the reflected beams. The effect of the second set of mirrors is to take the rays reflected by each of the first mirrors and reflect them into a small rectangle. This rectangle represents the approximate image of the point source at infinity. Both its height and width are determined by the mirror widths and the grazing angles of incidence. With x-rays, the mirror widths can be made very small before diffrac-

tion effects start widening the beam. Therefore, good resolution is possible.

Figure 1 shows the image of a small hole illuminated by 2537 Å radiation made by the multiple crossed-mirror system. The large area with thin white lines through it was produced by the direct beam; that is, by that portion of the incident beam that missed both of the mirror systems. Above this direct beam can be seen the area produced by the rays that were reflected by the first set of mirrors but that missed the second set. To the left of the direct beam is an area produced by the rays that hit the second mirror system but that missed the first. In the upper left hand corner is the spot formed by the light that struck both sets of mirrors; it represents the image of a small source.

To show that the system is capable of producing an image of an extended object, we illuminated an opening in the shape of a question mark. Its image formed by a multiple crossed-mirror system with four mirrors in each array and using white light is shown in Figure 2. The rays that experienced only single reflections can be identified by reference to the remarks made about Figure 1.

With this multiple crossed-mirror system the image of a distant point source resembles that produced by a rectangular pinhole since each crossing of two mirrors at right angles to one another presents effectively a small rectangular "window" for the radiation. From the point of view of total flux gathered, a system with n mirrors in each array is equivalent to n^2 pinholes, each pouring all its energy into the same spot.

The advantages of the system include simplicity of construction, approximately true point-to-point image-forming characteristics, absence of chromatic aberration, and speed (large flux gathering capabilities).

The second telescope is a contemplated improvement of the first to be made by curving the mirrors so that each one effectively becomes a section of a right-circular cylinder. The axes of all the cylinders would be parallel

to one another and perpendicular to the incoming beam. Curving the mirrors will greatly improve the resolving power of the system and the intensity of illumination at the image. At grazing incidence, spherical surfaces may be used instead of cylindrical ones with no practical loss in resolution as has been demonstrated by Kirkpatrick [1948, 1957] with reflection x-ray microscopes.

Spherical mirrors are easier to grind than cylindrical ones and are more stable than cylindrical mirrors made by bending flat plates in the manner of Ehrenberg [1947]. Experience with crossed-mirror systems in x-ray microscopy has shown that they can be effective even at wavelengths as short as 1.5 Å. Many of the restrictions on these systems are eased at longer wavelengths; therefore, the useful range of multiple crossed-mirror systems is likely to be 1 Å to 100 Å or beyond. A detailed summary of theoretical and experimental results will be submitted to the *Journal of the Optical Society of America*.

REFERENCES

- BAEZ, A. V., "A Self-supporting Metal Fresnel Zone-plate to Focus Extreme Ultraviolet and Soft X-Rays," *Nature*, 186, 953 (1960).
- EHRENBURG, W., "X-ray optics," *Nature*, 160, 330 (1947).
- FRIEDMAN, H., "Survey of Observations of Solar Ultraviolet and X-Rays," Symposium on Solar Emissions and the Interplanetary Medium, National Academy of Sciences, American Geophysical Union, April 28, 1960.
- KIRKPATRICK, P., AND BAEZ, A. V., "Formation of Optical Images by X-Rays," *J. Opt. Soc. Am.*, 38, 766 (1948).
- KIRKPATRICK, P. AND PATTEE, H. H., JR., "X-Ray Microscopy," *Handbuch der Physik. Encyclopedia of Physics* Vol. XXX (Edited by S. Flugge, Springer. Verlag, Berlin 1957).

ALBERT V. BAEZ

X-RAY VIEW OF THE PETROLEUM INDUSTRY

The petroleum industry may be broadly subdivided into four branches: producing, refining, transportation, and marketing. Ex-

ploration to find crude-petroleum reserves, drilling, and recovering petroleum from the underground reservoirs are all included in the term "producing." From one raw material, the petroleum industry manufactures hundreds of products through various refining processes. Transportation involves the handling, storage, and movement of raw materials and refinery products. Marketing puts these products into the hands of the ultimate consumer.

The raw material and the products of the petroleum industry consist mainly of liquid hydrocarbons. Although these hydrocarbons can be better studied by other methods, x-ray methods are useful in attacking a wide variety of problems in the petroleum industry. They are invaluable in the study and understanding of corrosion, which costs the industry more than five billion dollars annually. Impurities in hydrocarbon liquids and extraneous substances added to improve the properties of hydrocarbon products can be detected and measured by x-ray. Many refining processes involve solid reactions and materials, which can also be studied by x-ray.

Although x-ray diffraction has been used in studying crystal structures for a half-century, the use of x-ray methods in the petroleum industry as a routine analytical tool is relatively recent. A rapid growth in the use of diffraction, x-ray emission,¹ and absorption² is largely due to the availability of commercial diffractometers. Most of the commercial instruments originated from Friedman's design.³

More than a decade has passed since a comprehensive review⁴ of the application of x-ray methods to the petroleum industry was published.* In the intervening years, many new uses for this versatile technique have been found, especially in the producing and refining branches of the industry.

* The present review, except for revisions and updating of bibliography, was first published by the author in: *Norelco Reporter*, 5, 35 (1958).

Producing

With increasing demands for petroleum products, the need for finding new sources of raw petroleum is ever-increasing. Underground petroleum reserves are known to occur in certain geological formations and rock strata. In identifying and classifying rocks and geological formations, x-ray diffraction has been used to advantage.⁵ For example, the proportions of crystalline constituents of rocks can be determined by using the relative reflection intensities and the absorption coefficients of the pure crystalline components for calibration. X-ray emission spectrometry has been used to determine strontium and calcium in calcareous oil-bearing formations⁶; barium, titanium, and zinc in marine sediments⁷; and heavy metals in oil-field waters and brines.⁸

In drilling operations, x-ray diffraction can determine the nature of underground strata. In addition to rock analyses, certain types of clays can be characterized by x-ray diffraction.⁹ Some montmorillonite clays swell upon absorption of water from normal drilling fluids and tend to cave into the well being drilled. If such clays are promptly identified by x-ray, cave-in problems can be avoided by switching to an oil-base drilling fluid.

An oil reservoir contains three principal fluids: oil, gas, and water. The underground distribution of these fluids is important in determining the amount of petroleum that can be recovered from a reservoir. X-ray methods have been used to determine oil saturation and fluid distribution in reservoir-strata samples.¹⁰ By adding specific oil-soluble or water-soluble heavy-metal compounds as tracers, x-ray absorption can establish relationships between permeability and oil saturation in rock samples.

The crude petroleum from the well consists of gases and liquids. The separated gases may be sold as fuel or used in the manufacture of carbon-black. The petroleum industry is concerned chiefly with the liq-

uids, which are stored in field tanks for transportation to refineries where they are made into various products.

Refining

Refining processes may be broadly subdivided into three classes: separation, conversion, and finishing. The separation processes use such physical methods as distillation, extraction, and crystallization. Conversion processes use such chemical methods as cracking, reforming, coking, polymerization, alkylation, and isomerization. Finishing operations include elimination of impurities and addition of materials to improve product quality.

Separation. Separation processes generally divide the hydrocarbons into two phases. A liquid and a vapor phase are produced in distillation, two liquid phases in extraction, and a liquid and a solid phase in crystallization. In distillation and extraction processes, only indirect use can be made of x-rays, but they can be applied directly to processes involving solid crystalline substances.

Distillation. As a primary step in refining, hydrocarbon mixtures of different boiling ranges are separated by continuous fractional distillation. Because the products are liquids and vapors, such methods as infrared absorption and mass spectrometry are generally more useful than x-rays. However, one x-ray diffraction technique¹¹ permits identification of the heavier hydrocarbons by freezing them in a special cryostat. If the specimen chamber is cooled directly with liquid nitrogen, alkanes with carbon numbers as low as six may be frozen and studied by x-ray. A study of heavier arenes in the solid state¹² showed that even isomers could be characterized by their diffraction patterns. Further improvement in such techniques may provide a method for identifying petroleum hydrocarbons in the frozen state. However, in applying such powder-diffraction techniques to unknown mixtures

of hydrocarbons, extreme care is necessary to avoid anomalous interpretations.

Extraction. In extraction processes, a liquid solvent selectively dissolves and removes specific hydrocarbons from the liquid petroleum. Separation is easiest when the components differ widely in solubility, as arenes and alkanes do. A common example is the separation from lubricating oils of undesirable asphalts, which are insoluble in the solvent chosen. In extraction processes, x-ray methods offer little promise, except for the possible use of a frozen-sample technique. However, x-ray diffraction has been used to study colloidal asphaltene particles separated by solvent extraction from asphalts¹³; the similarity in spacing of the Debye reflections of these asphaltenes with those of basal graphite¹⁴ suggests a fundamental regularity in the arrangement of arene rings in these materials.¹⁵

Crystallization. Crystallization processes would appear to be a natural field for prolific x-ray work. However, because of interpretational difficulty of the powder-diffraction technique when applied to many hydrocarbons, x-ray methods have been used mainly in studying structures.

Lubricating oils are dewaxed by crystallization. The crystalline wax is separated by filtration at low temperatures and may be purified and marketed. The spacings between carbon atoms in solid paraffin waxes have been measured¹⁶ by x-ray diffraction. Hydrocarbons such as naphthalene, paraxylene, and cyclohexane can also be separated from petroleum streams by crystallization. Structural details of naphthalene have been clearly established by single-crystal diffraction.¹⁷

A recent process—clathrate separation—involves selectively complexing certain hydrocarbons with such crystals as urea, thiourea, and quinols. The clathrate crystals have channels, honeycombs, or cage-like spaces within their structures. Therefore, a mixture of hydrocarbon molecules that differ

in size or shape, but are otherwise similar, may be separated by introducing them into suitably sized and shaped spaces in the clathrate crystals. This process has been used for dewaxing petroleum streams, and for separating hydrocarbons with boiling points too close for separation by distillation. X-ray diffraction^{18, 19} showed that complexes of urea with various *n*-alkanes had identical structures different from that of uncomplexed urea. Details of urea-complex structures have been worked out by single-crystal diffraction.^{19, 20}

Conversion. Many of the products from the separation processes undergo some conversion before finishing for sale. The main purpose of conversion processes is to maximize the output of the most desirable gasoline components, in terms of both quality and quantity. In automobile engines, arenes and branched alkanes have better antiknock properties or higher "octane number" than *n*-alkanes. Therefore, most conversion processes are specifically designed to maximize these components.

With greater use of catalysts in these processes, x-ray methods have been of real service. X-ray diffraction studies of catalyst structures have led to better understanding of the mechanism of catalytic reactions and the role of the active component of the catalyst. Particle and crystallite sizes of catalysts are closely related to surface area and catalytic activity. Small-angle x-ray scattering permits measurement of catalyst particle size.²¹ Line broadening, measured in the back-reflection region and corrected for instrumental factors, has been used to determine catalyst crystallite size²² but is subject to errors due to non-uniform residual stresses in the crystal lattice.

Cracking. The earliest conversion process—cracking of heavier distillation products to gasoline—is still by far the most important. When large hydrocarbon molecules are heated to high enough temperatures and pressures, or activated by catalysts, they

tend to split or crack into smaller individual units. More than half of the crude petroleum processed in the United States is finally marketed as gasoline. The average crude petroleum yields about one-third its volume of gasoline by distillation, but this amount is doubled by cracking.

Because catalytic cracking leads to more gasoline of higher quality, it has almost completely replaced the older thermal process. Cracking catalysts may be used in the form of pellets in a stationary bed or as a fluidized bed of fine particles suspended in the vaporized hydrocarbon. Silica-on-alumina is the most common cracking catalyst, but silica-on-magnesia, acid-treated clays, and even blast-furnace slag have been used. Although x-ray methods are not used to determine the quality of the product, they have been used to measure impurities in catalysts and cracking feeds. X-ray emission methods have permitted rapid and quantitative determination of such trace impurities as iron, nickel, and vanadium in silica-on-alumina catalysts²³ or in cracking feeds.²⁴ Molybdenum and zinc in liquid petroleum have been determined by absorption-edge spectrometry²⁵; nickel in various petroleum liquids has been analyzed by x-ray emission methods, using cobalt as an internal standard.²⁶

Reforming. Reforming is a complex process in which dehydrogenation, cyclization, and isomerization are used to upgrade the gasoline obtained directly from distillation of crude petroleum. Because most arenes in the gasoline boiling range have octane numbers above 100, making more of them is the primary objective. As catalysts, molybdena and platinum, supported on alumina, are commonly used. Dehydrogenation—the main reaction—decreases the hydrogen:carbon ratio and liberates hydrogen as a useful by-product. Reforming also removes sulfur, which is often an undesirable impurity in petroleum.

X-ray emission has been applied to the rapid and accurate analysis of platinum-on-

alumina catalysts.²⁷ Absorption-edge spectrometry has been used to determine the amount of molybdena or platinum in catalysts.²⁸ Diffraction experiments in a reactor, transparent to X-rays, permitted the study of chemical interactions on metal-oxide catalysts *in situ*²⁸; the oxidation states of molybdena-on-alumina catalysts in reducing and oxidizing atmospheres were so determined. Sulfur-corrosion problems in reforming process equipment have also been studied by x-ray diffraction.

Coking. Destructive decomposition of the heavy residues from distillation of crude petroleum yields primarily a lighter fraction with a high hydrogen:carbon ratio and a heavier semisolid fraction with a low hydrogen:carbon ratio. The lighter material is suitable feed for catalytic cracking. The heavier material—coke—may be burned as fuel or sold as a by-product.

Both Bragg x-ray diffraction²⁹ and low-angle scattering³⁰ have contributed much to the understanding of the fundamental structure of coke. These methods have revealed the turbostratic layer structure of coke, and the increasing order that develops between the "graphite" layers as more hydrogen is lost at higher temperatures.

Other Processes. Polymerization recombines gaseous olefins from the catalytic cracking process to form a wide variety of products from gasoline components to solids used as plasticizers. Alkylation combines gaseous alkanes and olefins to produce branched isoalkanes, which are blended into gasolines. Isomerization converts low-octane *n*-alkanes to high-octane branched ones. Although important to the refiner, these three processes are not subject to direct x-ray study, except for equipment-corrosion problems associated with the use of corrosive acid catalysts.

Finishing. After separation and conversion, many products have to be further treated to impart desired properties. Such finishing operations usually involve either removal of some undesired component or

addition of some extraneous substance to alter physical or chemical behavior. In both the removal of impurities and the use of additives, x-ray methods have been used extensively.

Removal of Impurities. Sulfur, the most abundant impurity in petroleum, must be controlled to carefully specified levels in petroleum products. "Sweetening" processes eliminate or modify reactive or noxious sulfur compounds, such as mercaptans. Less-reactive sulfur compounds can be removed by catalytic desulfurization. X-ray methods have been proposed for checking sulfur levels of gasoline, fuel oils, and crude petroleum.

An x-ray emission spectrometer³¹ has been used to determine sulfur in gasoline and light hydrocarbons. Because of the long wavelength and high absorption of the characteristic x-ray spectrum from sulfur, the spectrometer was operated in a vacuum. The apparatus lacked the desired sensitivity; but by decreasing the distance between x-ray source and specimen, a nine-fold increase in sensitivity was anticipated.

Various x-ray absorption methods have been proposed for determining sulfur in fuel oils, crude petroleum, and other hydrocarbons. The hydrogen:carbon ratio affects these sulfur determinations. By using a sulfur-free hydrocarbon for reference or by using monochromatic x-ray, such effects upon the measured absorption can be minimized.

Several polychromatic absorption methods have been developed.^{32, 33, 34} An interesting technique³⁵ involves use of two x-ray beams from a single source, one passing through the sample, and the other through a reference hydrocarbon; it compares favorably in precision and accuracy with the more tedious chemical methods conventionally used. In determining sulfur in crude petroleum, absorption methods^{35, 36} are somewhat less precise because of the presence of impurities; however, the double-beam method³⁵ is claimed to be as accurate as standard chem-

ical methods. A novel method³⁷ makes use of K-capture x-rays from an Fe⁵⁵ source, instead of the usual generator; because of low equipment cost, this method may prove useful in controlling refinery operations despite low sensitivity. Recent comparison of the K-capture method with x-ray emission methods show that similar accuracy may be achieved, using either technique.³⁸

Monochromatic absorption methods can be made independent of hydrogen:carbon ratio by proper choice of x-ray wavelength. The mass absorption coefficients of hydrogen and carbon are equal at about 0.5 Å. A method involving use of the molybdenum K-alpha radiation at 0.71 Å approaches the accuracy of standard chemical methods.³⁹ Recently, greater accuracy was claimed for a similar technique based on fluorescent palladium K-alpha radiation at 0.59 Å.⁴⁰

Other impurities, such as nitrogen, oxygen, and highly unsaturated hydrocarbons that can oxidize to acids or polymerize to gums, are undesirable from the petroleum refiner's viewpoint. However, because of the low atomic number of the elements involved, x-ray methods are generally not applicable to them.

Use of Additives. Additives are used in gasolines, lubricating oils, and greases for different reasons. For example, some improve burning quality, some offset adverse effects of temperature on physical properties, and some prevent deterioration on prolonged storage. Best known is tetraethyllead (TEL), added to gasoline to control combustion and raise octane number.

Various x-ray methods have been developed to determine the TEL content of gasolines. Polychromatic absorption methods^{32, 33, 36, 41, 42} may be comparable in precision to chemical methods for gasolines of invariant composition. However, they suffer interference from such other elements as sulfur and the halogens; corrections must be applied or null techniques with a lead-free reference hydrocarbon must be used.

Absorption-edge spectrometry⁴³ using characteristic thorium x-ray lines, lying on either side of the lead-absorption discontinuity, is specific and independent of the matrix. The ratio of x-ray transmittances measured on both sides of the absorption edge is not affected by the matrix.^{35, 44} For determining TEL, the x-ray method⁴³ is less accurate but faster than chemical methods.

The use of x-ray emission spectrometry⁴⁵ for determining TEL in gasoline requires correction for hydrogen:carbon ratio or density of the hydrocarbons. This method has been used⁴⁶ for determining lead and bromine in aviation gasolines; by compensating for density and compositional variables in the hydrocarbon, or by using internal reference standards such as selenium,⁴⁷ precision can approach that of chemical methods.

Recently, use of manganese-carbonyl complexes have been suggested for enhancing the effect of TEL on octane quality of gasolines. A promising x-ray emission method, capable of detecting 0.1 gm Mn/gal of gasoline, appears to be as accurate as chemical analysis.⁴⁸

Additives in lubricating oils confer such desirable characteristics as detergency, resistance to oxidation, and temperature stability. Many of these additives are phosphates of alkaline-earth metals; and the rapid determination of such elements as barium, calcium, and zinc is needed for manufacturing control. X-ray emission methods,⁴⁹ with an accuracy similar to that of chemical methods, look promising for this application. An absorption method for determining zinc in lubricating oil has also been suggested.⁴²

Greases are intimate mixtures of lubricating oil and thickener. Thickeners may be soaps, non-soap organic crystalline compounds, modified silica, or even bentonite clays. Most greases consist of microscopic networks of thickener with oil held in the interstices. X-ray diffraction has been used to study the orientation and structures of

the thickener particles. Studies by the Schulz technique⁵⁰ show a variety of orientation distributions depending upon preparation methods, solids involved, and externally applied stress.⁵¹ X-ray diffraction has characterized metal soaps used as thickeners,⁵² and detected thermal phase transitions in them.⁵³ However, the powder-diffraction technique, normally used in such studies, needs care in interpretation because of the presence of disordered layer lattices⁵⁴; a sample having unchanging composition but different degrees of order, may give different diffraction patterns.

Other X-Ray Applications

X-ray methods are also used indirectly in the other two major branches of the petroleum industry—transportation and marketing. The storage, transportation, and distribution facilities are largely metal and are continuously subject to corrosion. In fact, the petroleum industry's corrosion problem begins at the oil well and continues to the tail-pipe of the automobile. Sulfur compounds and moisture are two major offenders. X-ray diffraction and spectrometry are fundamental tools in the study of corrosion problems.

After its products have reached the consumer, the petroleum industry must be concerned with how well they serve him. For example, in automotive engines, residues formed upon combustion can affect the operation or life of the engine through chemical or physical interaction. X-ray diffraction studies of such engine deposits⁵⁵ have revealed the nature of some of the problems and possible solutions to them. Absorption-edge spectrometry has been suggested⁵⁶ for determining lead and bromine in engine deposits. In studying the mechanism of lubrication, x-ray and electron-diffraction techniques are indispensable⁵⁶; boundary-lubrication films and the role of metal oxide-films in preventing metal-to-metal bonding

have been studied by diffraction methods.^{56, 57}

In recent years, petroleum has become an important source of organic chemicals. Petrochemicals, from natural gas and petroleum, number almost three thousand—with new products being added at the rate of four hundred per year.⁵⁸ Solvents, dyes, ammonia, sulfur, resins, rubbers, detergents, insecticides, anesthetics, explosives, thermosetting plastics, polymers, hydrogen, and carbon-black are just a few of the host. In the development and manufacture of some of these materials, x-ray diffraction has been especially useful. For example, in making such polymers as polyethylene or polypropylene, the ratio of crystalline to amorphous polymer must be controlled. This ratio can be determined by x-ray diffraction⁵⁹; elaborate instrumentation has been developed⁶⁰ for this purpose.

With a view to the future, the petroleum industry has extensively studied raw materials other than crude petroleum. Synthetic liquid fuels from hydrogenation of natural gas or coal have received much attention. Catalysts used in such syntheses have been advantageously studied by x-ray methods. For example, copper acts as an inhibitor in nickel catalysts in the Fischer-Tropsch process, but it is a promoter in ordinary hydrogenation reactions. X-ray-diffraction data on lattice parameters of co-precipitated nickel-copper catalysts suggest that a non-equilibrium state in the alloy phase may be responsible for this behavior.⁶¹ X-ray study of phase composition, dispersion, and lattice parameter of nickel-copper skeletal catalysts have led to understanding of catalytic-reaction mechanisms.⁶² A new iron carbide phase—FeC—found in the Fischer-Tropsch Synthesis reaction is believed to be an active component.⁶³

Conclusion

In the past decade, x-ray methods have played an increasingly important role in the

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petroleum industry. With further automation in the industry, x-ray methods for automatic and continuous process control may be visualized in future refineries. Increasingly complex refining processes, the mushrooming petrochemicals industry, and the processing of new raw materials will undoubtedly make stronger demands on the skill and ingenuity of the x-ray specialist.

REFERENCES

1. BIRKS, L. S., BROOKS, E. J., AND FRIEDMAN, H., *Anal. Chem.*, **25**, 692 (1953); H. A. LIEBHAFSKY, AND E. H. WINSLOW, *ibid.*, **28**, 583 (1956).
2. LIEBHAFSKY, H. A., *ibid.*, **25**, 689 (1953).
3. FRIEDMAN, H., *Electronics*, **18**, 132 (1945).
4. HUGHES, H. K., WILCZEWSKI, J. W., AND RATHER, J. B., JR., *Proc. Am. Petrol. Inst. Sect. III*, **28**, 85 (1948); G. M. WEBB, *Oil and Gas J.*, **45**, 203 (1947).
5. ALEXANIAN, C. L., *Rev. Inst. franc. petrole.*, **10**, 115 (1955).
6. LUCCHESI, C. A., *Anal. Chem.*, **29**, 370 (1957).
7. LEWIS, G. L., JR., AND GOLDBERG, E. D., *ibid.*, **28**, 1282 (1956).
8. KEHL, W. L., AND RUSSELL, R. G., *ibid.*, **28**, 1350 (1956).
9. BRINDLEY, G. W., "X-Ray Identification and Crystal Structure of Clay Minerals," The Mineralogical Society, London, 1951.
10. BOYER, R. L., MORGAN, F., AND MUSKAT, M., *Trans. A.I.M.E.*, **170**, 15 (1947); A. D. K. LAIRD, AND J. A. PUTNAM, Reports of Progress Fundamental Research on Occurrence and Recovery of Petroleum, A.P.I., 240 (1950-51); F. MORGAN, J. M. McDOWELL, AND E. C. DOTY, *J. Petrol. Technol.*, **2**, 183 (1950); L. B. LIPSON, *ibid.*, **3**, 19 (1951).
11. SMITH, H. N., AND HEADY, H. H., *Anal. Chem.*, **27**, 883 (1955).
12. HOFER, L. J. E., AND PEEBLES, W. C., *ibid.*, **23**, 690 (1951).
13. NELLENSTEYN, F. J., Science of Petroleum, (London), IV, 1938, page 2760 Assoc. Asphalt Technol. Proc. Tech. Sessions, 1937, page 78.
14. PFELFFER, J. PH., *De Ingenieur*, **54**, 41 (1939).
15. PFELFFER, J. PH., "The Properties of Asphaltic Bitumen," Elsevier (Amsterdam), 1950.
16. MULLER, A., *Proc. Roy. Soc. (London)* **A138**, 514 (1932); S. H. PIPER *et al.*, *Biochem. J.*, **25**, 2072 (1931); W. M. MAZEE, *Rec. Trav. Chim.*, **67**, 197 (1948).
17. ABRAHAMS, S. C., ROBERTSON, J. M., AND WHITE, J. G., *Acta Cryst.*, **2**, 233, 238 (1949).
18. BAILEY, W. A., *et al.*, *Proc. World Petrol. Congr.*, **3**, 161 (1951).
19. SMITH, A. E., *J. Chem. Phys.*, **18**, 150 (1950); A. E. SMITH, *Am. Chem. Soc. Div. Petrol. Chem. Symp.*, **33**, 5 (1955); H. SCHLENK, *ibid.*, **33**, 35 (1955).
20. BUERGER, M. J., *J. Appl. Phys.*, **17**, 579 (1946).
21. YUDOWITZ, K. L., *Anal. Chem.*, **25**, 721 (1953).
22. JELLINEK, M. H., AND FANKUCHEN, I., "Advances in Catalysis," **1**, 257 (1948).
23. DYROFF, G. V., AND SKIBA, P., *Anal. Chem.*, **26**, 1774 (1954).
24. DAVIS, E. N., HOECK, B. C., *ibid.*, **27**, 1880 (1955).
25. BARIEAU, R. E., *ibid.*, **29**, 348 (1957).
26. DWIGGINS, C. W., JR., AND DUNNING, H. N., *ibid.*, **31**, 1041 (1959).
27. GUNN, E. L., *ibid.*, **28**, 1433 (1956); A. I. LINCOLN, AND E. N. DAVIS, *ibid.*, **31**, 1317 (1959).
28. MOSEMAN, M. A., *J. Am. Chem. Soc.*, **73**, 5635 (1951).
29. RILEY, D. P., "The Ultrafine Structure of Coals and Coke," British Coal Utilization Research Association (Lond.), 1944.
30. GUINIER, A., *et al.*, "Small-Angle Scattering of X-Rays," J. Wiley and Sons, Inc. (New York) 1955.
31. BIRKS, L. S., *Rev. Sci. Instr.*, **22**, 891 (1951).
32. MOTTILAU, A. Y., AND DRIESENS, C. E., *Anal. Chem.*, **24**, 1852 (1952).
33. VOLTMAR, R. C., PETERSON, E. E., AND PETRUZZELLI, P. A., *ibid.*, **21**, 1491 (1949).
34. KEHL, W. L., AND HART, J. C., *Proc. Am. Petrol. Inst. Sect. III*, **28**, 9 (1948); S. W. LEVINE, AND A. H. OKAMOTO, *Anal. Chem.*, **23**, 699 (1951).
35. CRANSTON, R. W., MATHEWS, F. W. H., AND EVANS, N., *J. Inst. Petrol.*, **40**, 55 (1954).
36. ZEMANY, P. D., *et al.*, *Anal. Chem.*, **21**, 493 (1949).
37. HUGHES, H. K., AND WILCZEWSKI, J. W., *ibid.*, **26**, 1889 (1954).
38. DOUGHMAN, W. R., SULLIVAN, A. P., AND HIRT, R. C., *ibid.*, **30**, 1924 (1958).
39. HUGHES, H. K., AND WILCZEWSKI, J. W., *Proc. Am. Petrol. Inst. Sect. III*, **30M**, 11 (1950).
40. ECCLESTON, B. H., AND WHISMAN, M. L., *Anal. Chem.*, **28**, 545 (1956).
41. CALINGAERT, G., *et al.*, *ibid.*, **22**, 1238 (1950); S. W. LEVINE, AND A. H. OKAMOTO, *ibid.*, **23**, 1293 (1951).
42. ROBERT, L., AND ALEXANIAN, C. L., *Rev. Inst. franc. petrole*, **6**, 368 (1951).

43. HUGHES, H. K., AND HOCHSENGANG, F. P., *Anal. Chem.*, **22**, 1248 (1950).
44. FERRO, A., AND GALLOTTO, C. P., *Ann. Chim. (Rome)*, **45**, 1234 (1955).
45. LAMB, F. W., NIEBYLSKI, L. M., AND KIEFER, E. W., *Anal. Chem.*, **27**, 129 (1955).
46. BIRKS, L. S., *et al.*, *ibid.*, **22**, 1258 (1950); E. LÜSCHER, *Microchim. Acta.*, **2**, 696 (1955).
47. KOKOTAILO, C. T., AND DAMON, G. F., *Anal. Chem.*, **25**, 1185 (1953).
48. JONES, R. A., *ibid.*, **31**, 1341 (1959).
49. DAVIS, E. N., AND VAN NORDSTRAND, R. A., *ibid.*, **26**, 973 (1954); E. N. DAVIS, AND R. A. VAN NORDSTRAND, *ibid.*, **25**, 683 (1953).
50. SCHULZ, L. G., *J. Appl. Phys.*, **20**, 1030 (1949).
51. VOLD, M. J., *et al.*, *N. L. G. I. Spokesman*, **18**, 9 (1954) *J. Phys. Chem.*, **57**, 26 (1953).
52. BAUER, W. H., *et al.*, *Am. Chem. Soc. Abstr. of Papers 126th Meeting*, 6-7R (1954); R. D. VOLD, AND G. S. HATTIANGDI, *Ind. Eng. Chem.*, **41**, 2311 (1949).
53. VOLD, M. J., *et al.*, *Ind. Eng. Chem.*, **41**, 2539 (1949), *J. Am. Oil Chemists' Soc.*, **26**, 520 (1949).
54. STOSICK, A. J., *J. Chem. Phys.*, **18**, 1035 (1950).
55. LAMB, F. W., AND NIEBYLSKI, L. M., *Anal. Chem.*, **23**, 1388 (1951); F. W. LAMB, AND L. M. NIEBYLSKI, *J. Am. Chem. Soc.*, **75**, 511 (1953); D. S. PENNY, *Shell Aviation News*, No. 173, 14 (1952).
56. FINCH, G. I., *Brit. J. Appl. Phys. (Suppl. No. 1. Phys. of Lubrication, Part II)* **34** (1951).
57. FINCH, G. I., AND SPURR, R. T., *ibid.*, **79** (1951).
58. McGRATH, H. G., *Petroleum Processing*, **12**, 101 (1957).
59. AGGARWAL, S. L., AND TILLEY, G. P., *J. Polymer Sci.*, **18**, 17 (1955); S. KRIMM, *J. Phys. Chem.*, **57**, 22 (1953); G. NATTA, P. PINO, AND P. CORRADINI, *J. Am. Chem. Soc.*, **77**, 1708 (1955).
60. WALTER, N. M., Abstracts. Annual Meeting of the Am. Crystallographic Assn., Pittsburgh, Pa., 1957.
61. KADOTA, N., AND IKEDA, S., *J. Am. Chem. Soc.*, **73**, 4475 (1951).
62. SEVAST'YANOV, N. G., *Rentgen. Met. Issl. Prim. V. Khim. Goskhim* (1953), 85; A. M. RUBINSTEIN, *ibid.* (1953), 54; M. KEFALI, S. L. Lel'chuk *ibid.*, (1953), 78.
63. ECKSTROM, H. C., AND ADCOCK, W. A., *J. Am. Chem. Soc.*, **72**, 1042 (1950).

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